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**(54) MOLECULAR SIEVES FOR IMPROVED HYDROCARBON TRAPS**

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(56) References cited:  
**EP-A1- 0 716 877 EP-A1- 0 947 236**  
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**US-A- 5 482 692 US-A- 6 117 411**  
**US-A1- 2002 164 283**

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• **S.P.ELANGO VAN ET AL: "SSZ-33: A Promising  
Material for Use as a Hydrocarbon Trap", J. PHYS.  
CHEM. B., vol. 108, no. 35, 10 August 2004  
(2004-08-10), pages 13059-13061, XP002614097,  
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**EP 1 732 842 B1**

**Description****Technical Field**

**[0001]** This invention relates generally to molecular sieves and the use of such materials as hydrocarbon traps. Specifically, the invention relates to molecular sieves such as zeolites, and the use of such molecular sieves as adsorbents for hydrocarbon gases, especially exhaust gases such as are formed during the combustion of hydrocarbons, and more particularly to the adsorption of hydrocarbon gases formed during the cold start operation of an internal combustion engine.

**Background of the Invention**

**[0002]** Future low emissions standards for vehicles are forcing automobile and catalyst manufacturers to focus on reducing cold start hydrocarbon emissions since a large portion of hydrocarbon emissions occur during the cold start period. Consequently, control of emissions during the cold start operation of a vehicle containing an internal combustion engine is essential. Vehicles equipped with a conventional three-way catalytic converter typically contain precious metals supported on a washcoat layer, which in turn is deposited on a monolithic carrier. Fresh catalysts start to operate at about 170°C, while aged catalysts work only at about 200-225°C. These catalysts usually require at least 1-2 min to reach such temperatures, and during this "cold start" period, 70-80% of the tailpipe hydrocarbon emissions occur. Such cold start emissions often result in failure in the cycle of the U.S. federal test procedure (FTP), a standardized laboratory method for new vehicles testing that is based on two simulated environments; namely, city and highway, in which prototypes of new vehicle models are driven by a trained driver in a laboratory on a dynamometer. At lower temperatures where the catalyst in a catalytic converter is not able to effectively convert incompletely burned hydrocarbons to final combustion products, a hydrocarbon adsorber system should trap hydrocarbons exhausted from the engine before they reach the catalytic converter by adsorbing the incompletely burned hydrocarbons. In the ideal case, desorption should occur at temperatures exceeding catalyst light-off.

**[0003]** The critical factors for any emission hydrocarbon trap are the adsorption capacity of the adsorbent, the desorption temperature at which adsorbed hydrocarbons are desorbed and passed to the catalytic converter (must be higher than the catalyst operating temperature), and the hydrothermal stability of the adsorbent. Molecular sieves such as zeolites have generally been found to be useful adsorbents for this application in part due to their hydrothermal stability under these conditions compared to other materials.

**[0004]** Various studies have focused on the use of molecular sieves, and zeolites in particular, as adsorbents, including medium and large pore zeolites, although, in some cases, the types of molecular sieves or zeolites used have not been identified. A series of zeolites ( $\beta$ , ZSM-5, mordenite, and Y) have been investigated in such studies for their hydrocarbon adsorption capacity under a variety of conditions (see, e.g., Burke, N. R.; Trimm, D. L.; Howe, R. F. Appl. Catal., B 2003, 46, 97; Lafyatis, D. S.; Ansell, G. P.; Bennett, S. C.; Frost, J. C.; Millington, P. J.; Rajaram, R. R.; Walker, A. P.; Ballinger, T. H. Appl. Catal., B 1998, 18, 123; Noda, N.; Takahashi, A.; Shibagaki, Y.; Mizuno, H. SAE Tech. Pap. Ser. 1998, 980423; and, Czaplewski, K. F.; Reitz, T. L.; Kim, Y. J.; Snurr, R. Q. Microporous Mesoporous Mater. 2002, 56, 55)

**[0005]** Previous investigations have thus far found zeolite- $\beta$  to be a promising material for this application. However, aged zeolite- $\beta$  catalysts demonstrate degraded performance in trapping hydrocarbons due to low hydrothermal stability when used as an exhaust gas adsorbent. Hence, despite advances in the art, an important need continues to exist for a material that possesses a better adsorption capacity, higher desorption temperature, and hydrothermal stability than current adsorbents such as zeolite- $\beta$  for use in emission control, particularly during the cold start operation of an internal combustion engine.

**[0006]** WO 02/07859 A2 discloses a hydrocarbon trap or catalyst composition comprising a hydrocarbon-adsorbing material and an active metal from potassium, rubidium, caesium, beryllium, magnesium, calcium, barium or strontium, or a mixture of any two or more thereof, characterised in that the active metal is impregnated on the material.

**[0007]** EP 0 716 877 A1 discloses a combined catalyst hydrocarbon trap for the treatment of the exhaust gas of an engine, which comprises (1) an underlayer comprising absorber, which includes zeolite of silica to alumina weight ratio of greater than 300, and (2) an overlayer, arranged over the underlayer, which comprises catalyst on a support which does not absorb the hydrocarbon preferentially compared to water, the catalyst being catalytically active for the conversion of the hydrocarbon to carbon dioxide and water.

**[0008]** EP 0 947 236 A1 discloses a catalysed hydrocarbon trap material washcoat used in a trap. The material comprises palladium and silver dispersed on a high surface area metal oxide support and a zeolite material such as one or more of ZSM-5, Beta, Y and other suitable zeolites.

**Summary of the Invention**

**[0009]** The present invention is addressed to the aforementioned needs in the art, and provides a novel and improved

method for treating an exhaust gas that comprises a hydrocarbon product resulting from incomplete combustion of a hydrocarbon fuel. According to claim 1 a method of treating exhaust gas that comprises a hydrocarbon product is provided, the method comprising contacting the exhaust gas with a CON topology molecular sieve for a time period effective to facilitate adsorption of the hydrocarbon product by the molecular sieve; passing a purge gas through the molecular sieve to remove adsorbed hydrocarbon product therefrom; and contacting the purge gas containing the removed hydrocarbon product with a hydrocarbon conversion catalyst.

[0010] In another aspect of the invention, a system according to claim 18 for treating exhaust gases formed during the combustion of a hydrocarbon is provided, the system comprising an exhaust gas adsorption unit containing an adsorbent CON topology molecular sieve; a catalytic converter unit containing a hydrocarbon conversion catalyst; means for supplying an exhaust gas comprising a hydrocarbon product to the adsorption unit so that the hydrocarbon product is at least partly adsorbed by the molecular sieve; means for transferring the hydrocarbon product from the adsorption unit to the catalytic converter unit wherein the hydrocarbon product is converted to an exhaust emission gas; and means for exhausting the exhaust emission gas from the catalytic converter unit.

## **Brief Description of the Drawings**

[0011]

FIG. 1A and FIG. 1B illustrate toluene desorption profiles for certain molecular sieves, as described in Example 1.

FIG. 2 depicts the toluene desorption profile for zeolite- $\beta$ (1540), zeolite- $\beta$ (40), and zeolite- $\beta$ (100) as a function of temperature, as described in Example 2.

FIG. 3 provides a comparison between the toluene desorption characteristics for fresh, non-aged zeolite- $\beta$  and SSZ-33 and the same zeolites hydrothermally aged in 10 wt.% water vapor at 800°C for about 5 hours.

FIG. 4 depicts X-ray powder diffraction patterns for SSZ-33 and zeolite- $\beta$ (100) before and after hydrothermal treatment.

FIG. 5 illustrates the toluene desorption capacity for SSZ-33 and zeolite- $\beta$  before and after hydrothermal treatment.

FIG. 6 shows the effects of differing temperature hydrothermal treatment conditions on the toluene desorption characteristics of zeolite- $\beta$ (100).

FIG. 7 shows the amount of toluene desorbed over zeolite- $\beta$ (100) hydrothermally treated at different temperatures.

FIG. 8 depicts X-ray powder diffraction patterns for zeolite- $\beta$ (100) hydrothermally treated at different temperatures.

FIG. 9 illustrates the toluene desorption profiles of SAPO-5 hydrothermally treated at different temperatures.

FIG. 10 depicts the toluene desorption profile for zeolite- $\beta$ (100) and SAPO-5 hydrothermally treated at 600°C.

FIG. 11 shows a comparison of the amount of toluene desorbed over zeolite- $\beta$ (100) and SAPO-5 for samples hydrothermally treated at 600°C.

FIG. 12 illustrates the toluene desorption profile of SSZ-33 at different desorption rates.

FIG. 13 illustrates the amount of toluene desorbed over SSZ-33 at different desorption rates.

FIG. 14 shows the toluene desorption profiles for Ag-zeolite- $\beta$ (100) before and after hydrothermal treatment at 800°C.

FIG. 15 shows the X-ray powder diffraction patterns for Ag-zeolite- $\beta$ (100) and Ag-zeolite- $\beta$ (40) before and after hydrothermal treatment.

FIG. 16 shows the toluene desorption profiles for SSZ-33 and Ag-SSZ-33.

FIG. 17 shows the toluene desorption profiles for SAPO-5 and Ag-SAPO-5.

FIG. 18 depicts the X-ray powder diffraction patterns for SSZ-33, Ag-SSZ-33, SAPO-5, and Ag-SAPO-5.

FIG. 19 shows the toluene desorption profiles for Ag exchanged SSZ-33, zeolite- $\beta$ (40), and SAPO-5.

FIG. 20 show SEM photomicrographs of certain zeolites hydrothermally treated at 800°C in which particle agglomeration is evident.

## **Detailed Description of the Invention**

[0012] It is to be understood that unless otherwise indicated this invention is not limited to specific materials or reactants, reaction conditions, or the like, as such may vary. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only and is not intended to be limiting.

[0013] In this specification and in the claims that follow, reference will be made to a number of terms, which are intended to have the following meanings:

[0014] As used in the specification and the appended claims, the singular forms "a," "an" and "the" include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to "a molecular sieve" or "a hydrocarbon combustion product" encompasses a combination or mixture of different molecular sieves or hydrocarbon combustion product compounds as well as a single molecular sieve or hydrocarbon compound. Similarly, the phrases "a mixture thereof" and "mixtures thereof" includes mixtures of one or more of the same category of referent, as well as

mixtures of different referents. For example, the combination of a hydrocarbon combustion product and a molecular sieve is intended to include mixtures of one or more combustion products with one or more molecular sieves, in addition to a mixture of one combustion product and one molecular sieve.

**[0015]** The phrase "characterized by" generally refers to a description of a characteristic or property rather than a particular method of characterizing the property or determining the characteristic. For example, in one aspect as discussed below, the invention may be described in terms of the molecular sieve characteristics in which the CON topology molecular sieve is characterized by an increased adsorption capacity or an increased desorption temperature compared to the non-CON topology molecular sieve. By this it is meant that the CON topology molecular sieve demonstrates such properties without reference to a specific technique for determining the degree of improvement.

**[0016]** The term "CON topology molecular sieve" as used herein refers to molecular sieves known in the art as having the framework structure designated as "CON" by the Nomenclature Committee of the International Zeolite Association (IZA). Similarly, the term "non-CON topology molecular sieve" refers to molecular sieves known in the art as having a framework structure other than those molecular sieves designated as "CON" by the Nomenclature Committee of the International Zeolite Association. Specific detailed information concerning the structure and nomenclature of molecular sieves including CON topology zeolites and other non-CON topology zeolites may be obtained from the Structure Commission of the IZA, or from the IZA website located at <http://www.iza-structure.org/databases/>.

**[0017]** The phrase "improved adsorption" is not intended to be particularly limited and generally refers to the ability of the CON topology molecular sieve to provide improved adsorption properties relative to a non-CON topology molecular sieve.

**[0018]** The phrase "method of treating exhaust gas" generally refers to a method of reducing the emission of exhaust gas pollutants, particularly those associated with the incomplete combustion of hydrocarbon fuels. The treatment method is primarily directed to reducing the emission of incompletely combusted exhaust gas components, such as occur during the cold start operation of an internal combustion engine.

**[0019]** As noted above, a method of treating exhaust gas that comprises a hydrocarbon product is provided, the method comprising contacting the exhaust gas with a CON topology molecular sieve for a time period effective to facilitate adsorption of the hydrocarbon product by the molecular sieve; passing a purge gas through the molecular sieve to remove adsorbed hydrocarbon product therefrom; and contacting the purge gas containing the removed hydrocarbon product with a hydrocarbon conversion catalyst. Although the use of adsorbent materials in exhaust gas systems is generally known, the present invention provides an improvement over the use of such prior adsorbents due to the use of an adsorbent material that comprises a CON topology molecular sieve.

**[0020]** The method may be applied as a batch process in which the adsorbent is contacted with the exhaust gas batchwise or as a continuous or semi-continuous process in which the exhaust gas continuously or semi-continuously flows through the molecular sieve. For example, the method may be applied as a continuous process for purifying the exhaust gas from an internal combustion engine in which a hydrocarbon fuel is combusted. In such a continuous process, the exhaust gas may be first passed from the source, such as from an internal combustion engine, to an adsorbent molecular sieve having a CON topology, so that components in the exhaust gas, particularly hydrocarbons, are adsorbed by the molecular sieve. Depending on the application, the adsorbed components are typically subsequently desorbed from the molecular sieve and brought into contact with a catalyst. In the case of an exhaust gas purification system, the CON topology molecular sieve may be utilized to adsorb partially combusted hydrocarbon components from the exhaust gas of an internal combustion engine by contacting the molecular sieve with the exhaust gas upstream of a catalytic converter. As the molecular sieve and the catalyst subsequently heat up due to continued throughflow of the exhaust gas, the components adsorbed onto the molecular sieve are desorbed into the exhaust gas stream and passed on to the converter. The desorbed hydrocarbon components are then converted by the catalyst due to the improved hydrocarbon conversion efficiency of the catalyst at higher operating temperatures.

**[0021]** The method of the invention may also be carried out sequentially and continuously with a flowing exhaust gas, that is, wherein the exhaust gas continuously flows through the molecular sieve and then through a downstream catalytic converter. In this regard, the exhaust gas may also essentially function as the purge gas for removing exhaust components desorbed from the molecular sieve. A separate purge gas stream, or a separate purge gas stream in conjunction with the exhaust gas stream, may also be used to remove the desorbed exhaust gas components, including, without limitation, air such as secondary air that is added to the exhaust gas stream, an inert gas, or a mixture thereof.

**[0022]** The use of the CON topology molecular sieve in batch and semi-continuous systems is also within the scope of the invention. For example, in a batch process the CON topology molecular sieve may be contacted with a portion of the exhaust gas such that the exhaust gas components, particularly incompletely combusted hydrocarbon components produced during cold start operation of an internal combustion engine, are adsorbed onto the molecular sieve. Thereafter, when the operating temperature of a catalyst such as in a catalytic converter has been reached, the adsorbed components may be purged using a purge gas and passed to the catalyst for conversion to exhaust gas emission products. Similarly, in a semi-continuous process, the exhaust gas may be initially passed through the molecular sieve and subsequently through a downstream catalyst. After a period of time (e.g., when the catalyst light-off temperature is reached), the

exhaust gas may be re-directed to pass only through the catalyst, such that the molecular sieve is bypassed. A purge gas such as air may then be passed through the molecular sieve to desorb the exhaust gas components adsorbed onto the molecular sieve.

**[0023]** Although the molecular sieve may be utilized to adsorb exhaust gas components by itself, it may also be utilized in an adsorbent material that comprises the molecular sieve along with additional materials such as binders and clays. The adsorbent material may also comprise one or more catalysts in conjunction with the molecular sieve. Such catalysts are generally known in the art and are not specifically limited for use herein in conjunction with the adsorbent material. Other adsorbent materials may also be included along with the CON topology molecular sieve if desired, including without limitation molecular sieves other than CON topology molecular sieves, such as, e.g., SSZ-23, SSZ-31, SSZ-35, SSZ-37, SSZ-41, SSZ-42, SSZ-43, SSZ-44, SSZ-45, SSZ-47, SSZ-48, SSZ-53, SSZ-54, SSZ-55, SSZ-57, SSZ-58, SSZ-59, SSZ-60, SSZ-63, SSZ-64, SSZ-65, and mixtures thereof

**[0024]** In general, any molecular sieve having a CON topology is intended to be suitable for use in the invention. While not intended to be limited thereto, suitable examples of CON topology molecular sieves include, in one embodiment, silicate molecular sieves such as SSZ-33, SSZ-26, CIT-1 and mixtures thereof. The structural characteristics, x-ray diffraction pattern data, and methods for preparing these molecular sieves are described in numerous publications and patents and need not be detailed herein. See, e.g., U.S. Pat. Nos. 4,910,006 (for SSZ-26 to Zones et al.); 4,963,337 (for SSZ-33 to Zones et al.); 5,512,267 (for CIT-1 to Davis et al.); Jones, C. W.; Zones, S. I.; Davis, M. E.; *Microporous and Mesoporous Materials*, 1999, 28, 471.

**[0025]** As is known in the art, CON topology molecular sieves contain 10- and 12-membered ring (MR) pores in which the 10- and 12-MR channels intersect and connect to form a large void volume at the intersections. While not intending to be bound thereby, it is believed that the porosity of CON topology molecular sieves provides beneficial adsorption properties, in part since transport of diffusing molecules can occur in the 12-ring pore system, the 10-ring pores, or in both types of pores. As discussed in the Examples provided below, such beneficial characteristics are demonstrated over non-CON topology molecular sieves, particularly over zeolite- $\beta$ , zeolite-Y, mordenite, and ZSM-5 measured under the same conditions and according to the same hydrothermal treatment.

**[0026]** The CON topology molecular sieve is selected to provide improved adsorption of the hydrocarbon product compared to a non-CON topology molecular sieve before and/or after the same hydrothermal treatment of the CON topology molecular sieve and the non-CON topology molecular sieve. While not necessarily limited thereto, such hydrothermal treatments are generally intended to simulate the conditions experienced in an exhaust gas emission system. For example, as discussed in the examples, suitable hydrothermal treatment of the CON topology molecular sieve and the non-CON topology molecular sieve may be carried out in the presence of 10 wt.% water vapor at 800°C for about 5 hours in a stream of air at 25 mL/min.

**[0027]** The improved adsorption of the hydrocarbon product by the CON topology molecular sieve may be demonstrated by a number of beneficial adsorption characteristics of the CON topology molecular sieve. For example, the improved adsorption may be characterized by an increased adsorption capacity or an increased desorption temperature compared to the non-CON topology molecular sieve. The CON topology molecular sieve may, of course, also demonstrate both an increased adsorption capacity and an increased desorption temperature compared to the non-CON topology molecular sieve. In particular, in one aspect, the increased adsorption capacity of the CON topology molecular sieve may be at least 1.1 times the adsorption capacity of the non-CON topology molecular sieve, more particularly, at least 1.2 times the adsorption capacity of the non-CON topology molecular sieve, and still more particularly, at least 1.25 times the adsorption capacity of the non-CON topology molecular sieve.

**[0028]** The CON topology molecular sieve may comprise a framework heteroatom such as Al, B, Ga, Fe, Zn, Mg, Co, and mixtures thereof in addition to Si. The CON topology molecular sieve may also contain a metal cation selected from rare earth, Group 2 metals, Groups 8-10 metals, and mixtures thereof, e.g., the metal cation may be selected from Mn, Ca, Mg, Zn, Cd, Pt, Pd, Ni, Co, Ti, Al, Sn, Fe, Co, and mixtures thereof.

**[0029]** In an alternate embodiment, the CON topology molecular sieve comprises a CON topology molecular sieve that contains a metal selected from Cu, Ag, Au and mixtures thereof. For example, a CON topology molecular sieve such as SSZ-33 may at least partially contain Ag incorporated by exchange (e.g., designated as Ag-SSZ-33) according to techniques described in the art. See, e.g., Liu, X.; Lampert, J. K.; Arendarskiia, D. A.; Farrauto, R. J.; *Applied Catalysis B: Environmental* 2001, 35, 125.

**[0030]** CON topology silicate molecular sieves such as CON topology zeolites may also include other partial replacement atoms for Si such as Ge. Techniques for replacing Si with Ge are known in the art, e.g., as described by Zones et al. in a number of patents (see U.S. Pat. Nos. 4,910,006 and 4,963,337). While not necessarily limited thereto, such silicate molecular sieves may be generally classified as high silica molecular sieves, i.e., silicates in which the ratio of Si to Al, Si/Al > 5.

**[0031]** Exhaust gases produced from the combustion of a hydrocarbon fuels in an internal combustion engine contain a plurality of combustion components, typically including linear and branched chain non-aromatic hydrocarbons, cycloaliphatic hydrocarbons, aromatic hydrocarbons, polycyclic hydrocarbons and mixtures thereof, as well as non-hydro-

carbon components such as carbon dioxide, water, nitrogen oxides and sulfur dioxide. Included within such emissions compounds are aromatic hydrocarbons such as toluene, xylene, benzene and mixtures thereof; linear and branched hydrocarbons such as methane, ethane, ethylene, propane, propylene, butane, pentane, hexane, heptane, octane; cycloaliphatic hydrocarbons such as cyclohexane; and additional fuel additives such as alcohols and methyl tertiary butyl ether (MTBE). The method of the invention may be advantageously utilized to reduce such hydrocarbon emissions, particularly during cold start operation of an internal combustion engine, without being necessarily limited to a particular hydrocarbon fuel. Typical hydrocarbon fuels benefiting from the present invention include gasolines, diesel fuels, aviation fuels, and the like.

**[0032]** As noted, the invention also relates to an exhaust system for treating exhaust gases formed during the combustion of a hydrocarbon. While a number of configurations are possible in which a CON topology molecular sieve is utilized as the hydrocarbon adsorbent, in general the exhaust system comprises an exhaust gas adsorption unit containing an adsorbent CON topology molecular sieve; a catalytic converter unit containing a hydrocarbon conversion catalyst; means for supplying an exhaust gas comprising a hydrocarbon product to the adsorption unit so that the hydrocarbon product is at least partly adsorbed by the molecular sieve; means for transferring the hydrocarbon product from the adsorption unit to the catalytic converter unit wherein the hydrocarbon product is converted to an exhaust emission gas; and means for exhausting the exhaust emission gas from the catalytic converter unit.

**[0033]** Both the adsorption unit and the catalytic converter may be any suitable devices known in the art, provided the adsorbent material contained in the adsorption unit comprises a CON topology molecular sieve. Without limitation, any catalyst suitable for converting incompletely combusted fuel products to final exhaust gas emission products such as water and carbon dioxide may be used. Suitable means for transferring the hydrocarbon product from the adsorption unit to the catalytic converter and for exhausting the exhaust emission gas from the catalytic converter unit generally include any known device used in exhaust gas systems. Although any suitable material may be utilized, in the area of vehicle exhaust gas systems such devices typically are metal or other piping and tubes, and the like,

**[0034]** It is to be understood that while the invention has been described in conjunction with certain specific embodiments thereof, that the foregoing description as well as the examples that follow are intended to illustrate and not limit the scope of the invention. Other aspects, advantages and modifications within the scope of the invention will be apparent to those skilled in the art to which the invention pertains.

## **Experimental**

**[0035]** In the following examples, efforts have been made to ensure accuracy with respect to numbers used (e.g., amounts, temperature, etc.) but some experimental error and deviation should be accounted for. Unless indicated otherwise, temperature is in degrees C and pressure is at or near atmospheric.

**[0036]** All materials used were either prepared according to procedures detailed in the literature or were obtained from commercially-available sources. Zeolites  $\beta$  ( $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 100, abbreviated below as "zeolite- $\beta$  (100)"), mordenite ( $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 10.2, abbreviated below as "mordenite (10.2)"), and ZSM-5 ( $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 23.8, abbreviated below as "ZSM-5 (23.8)") were obtained from Tosoh Corporation and zeolite Y ( $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 5.6, abbreviated below as "zeolite-Y

(5.6)") was supplied by Catalysts & Chemicals Ind. Co., Ltd. All materials used in this study were in the H-form, and they were obtained by a 3-fold ion-exchange with 0.1 M ammonium nitrate solution.

**[0038]** SSZ-33 was synthesized, and posttreatment was carried out according to the procedure reported in the literature (see, e.g., Dartt, C. B.; Davis, M. E. Appl. Catal., A 1996, 143, 53). After the treatment, the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio was found to be 60.

**[0039]** The temperature-programmed desorption (TPD) of toluene was used to investigate the desorption characteristics of zeolites and was carried out by using a gas chromatograph (GC from Shimadzu model GC-9A) with a thermal conductivity detector (TCD). A sample of ca. 50 mg was placed in a quartz tube of 4 mm i.d., between quartz wool. Subsequently, the sample was activated in a flow of helium at 300°C for about 2 h. After cooling the column to a temperature of 50°C, toluene was injected using a pulse method with 2  $\mu\text{L}$  pulses until saturation. Desorption was performed by a 90°C hold method in which the column was heated from 50 to 90°C at a heating rate of 20K/min and maintained at the same temperature for about 10 min to desorb weakly adsorbed toluene. Subsequently, the samples were heated to 390°C at the rate of 20K/min and kept at 390°C for an additional 10 min and then cooled to room temperature. All the TPD experiments were carried out under a flow of helium with a flow rate of 50 mL/min.

## **Example 1**

### **Toluene desorption profiles for zeolite-Y(5.6), Mordenite (10.2), ZSM-5, Zeolite- $\beta$ and SSZ-33**

**[0040]** The toluene desorption for zeolite-Y ( $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 5.6), Mordenite ( $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 10.2) and ZSM-

5 were carried out according to the TPD procedures described above at a rate of 5K/min. As shown in FIG. 1A, the toluene desorption profiles for these zeolites vary from a low desorption rate for ZSM-5 to higher rates for zeolite-Y(5.6) and Mordenite (10.2). However, all of zeolites Zeolite Y, ZSM-5, and mordenite desorb toluene at a relatively low temperature. In FIG 1B, SSZ-33 demonstrated desorption characteristics superior in performance over the other zeolites used. The end temperature of toluene desorption decreases in the following order; SSZ-33 >  $\beta$  > mordenite > Y > ZSM-5. Without wishing to be bound by such possible conclusions, in comparison to the materials used in this study, SSZ-33 shows an enhanced high-temperature desorption over the other zeolites that may be ascribed to the larger amount of toluene adsorbed. In particular, SSZ-33 exhibits two sharp maxima at ca. 150 and 200°C. It is possible that this behavior may be ascribed to the unique pore system of SSZ-33 in which desorption from the 10-MR (multi-ring) channel occurs at a relatively higher temperature, but further studies are needed in order to understand the reasons for this behavior. From these results, SSZ-33 and zeolite- $\beta$  were chosen for a more detailed comparison of the adsorption characteristics and zeolite hydrothermal stability.

## Example 2

### Toluene desorption profiles for zeolite- $\beta$ (1540), zeolite- $\beta$ (40), and zeolite- $\beta$ (100)

[0041] In order to better understand the toluene desorption characteristics of zeolite- $\beta$ , the toluene TPD behavior of three beta zeolites having different  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios were studied as described above. As shown in FIG. 2, the toluene desorption profile for zeolite- $\beta$ (1540), zeolite- $\beta$ (40), and zeolite- $\beta$ (100) as a function of varies with the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios (listed in parentheses). From this information, zeolite- $\beta$ (100) was chosen as a comparison standard over the other beta zeolites since the adsorption capacity and end desorption temperature are both superior to the other two beta zeolites.

## Example 3

### Hydrothermal treatment effect on toluene desorption profiles for zeolite- $\beta$ (100) and SSZ-33

[0042] As described above, the TPD toluene desorption profiles for SSZ-33 and zeolite- $\beta$ (100) were determined for samples before and after hydrothermal treatment (10 wt.% water vapor at 800°C for about 5 hours). As shown in FIG. 3, both unaged (fresh) and hydrothermally treated SSZ-33 provided superior desorption characteristics, specifically SSZ-33 and the same zeolites hydrothermally aged in 10 wt.% water vapor at 800°C for about 5 hours.

## Example 4

### X-ray powder diffraction of zeolite- $\beta$ (100) and SSZ-33

[0043] The X-ray powder diffraction patterns of zeolite- $\beta$ (100) and SSZ 33 were obtained as shown in FIG. 4 for SSZ-33 and zeolite- $\beta$ (100) before and after hydrothermal treatment. From these patterns, little or no change was seen implying that no significant structural changes occurred in the zeolites due to the hydrothermal treatment.

## Example 5

### Toluene adsorption capacity for SSZ 33 and zeolite- $\beta$ before and after hydrothermal treatment

[0044] The toluene adsorption capacity of SSZ 33 and zeolite- $\beta$  was also determined as shown in FIG. 5 for samples before and after hydrothermal treatment (according to the conditions described above). From this figure, the toluene desorption capacity of SSZ-33 is superior to zeolite- $\beta$  both before and after hydrothermal treatment, in particular the capacity of SSZ-33 is about 1.25 times larger than that of zeolite- $\beta$ . The capacity and the desorption temperature of SSZ-33 are superior to those of zeolite- $\beta$  when considering the requirements in a hydrocarbon cold trap application. There is a decrease in the adsorption capacity after hydrothermal treatment of SSZ-33. The total amount desorbed from the fresh SSZ-33 is 1.82 mmol/g and is decreased to 1.60 mmol/g after the hydrothermal treatment. By comparison with zeolite- $\beta$ , the desorption from a fresh sample amounts to 1.49 mmol/g, while after the hydrothermal treatment it is only 0.56 mmol/g.

[0045] Table 1 presents the micropore volume of these samples as measured by nitrogen adsorption. SSZ-33 possesses a micropore volume of 0.21  $\text{cm}^3/\text{g}$  which is not decreased after hydrothermal treatment while for zeolite- $\beta$  the micropore volume is decreased to 0.16  $\text{cm}^3/\text{g}$  from 0.20  $\text{cm}^3/\text{g}$ .

TABLE 1: Sample Micropore Volume and Crystal Size

sample	Micropore Volume (cm <sup>3</sup> /g)	Crystal Size (as determined by SEM) (μm)
SSZ-33	0.21	1-2
SSZ-33, aged	0.21	
zeolite-β	0.20	<1
zeolite-β, aged	0.16	

**Example 6****Hydrothermal treatment of zeolite-β(100) and SAPO-5 at different temperatures**

[0046] The toluene desorption characteristics of zeolite-β(100) were further determined by hydrothermally treating zeolite-β at different temperatures (600, 700 and 800°C under the above conditions of water vapor and treatment times) as shown in FIG. 6. From this figure, hydrothermal treatment at 700°C exhibits better desorption performance than the zeolite-β(100) treated at 600°C. FIG. 7 also shows the toluene adsorption capacity of zeolite-β(100) at different temperatures (600, 700 and 800°C under the above conditions of water vapor and treatment times). FIG. 8 further provides the X-ray powder diffraction patterns for zeolite-β(100) treated at the different temperatures and shows that no significant structural changes occurred in the samples due to the hydrothermal treatment. FIG. 9 illustrates the toluene desorption profiles of SAPO-5 hydrothermally treated also at different temperatures (600, 700 and 800°C as above).

[0047] FIG. 10 further depicts the toluene desorption profile for zeolite-β(100) and SAPO-5 hydrothermally treated at 600°C, and FIG. 11 shows the desorbed amount of toluene for each of these zeolites, indicating that zeolite-β(100) provides better adsorption capacity and desorption performance than SAPO-5.

**Example 7****Comparison of desorption characteristics of SSZ-33 at different desorption rates**

[0048] FIGs. 12 and 13 present the results of an investigation of the desorption characteristics of SSZ-33 at different desorption rates, respectively, the desorption profile and the desorption capacity. From these figures, the toluene desorption temperature is observed to increase with the increase in the rate of desorption.

**Example 8****Desorption characteristics of SSZ-33, zeolite-β(100), and SAPO-5 with Ag exchanged zeolites**

[0049] Because the incorporation of Ag may lead to an increase in hydrocarbon adsorption in zeolites, the desorption characteristics of Ag exchanged zeolite compared to the unmodified zeolite was investigated. Silver exchange over zeolite-β(100), SSZ-33, and SAPO-5 was carried out by a conventional ion-exchange method by combining 1g AgNO<sub>3</sub> with 100g H<sub>2</sub>O and 1g sample under stirring for 24 hr at 80°C, followed by filtering and rinsing, drying, and heating at 400°C in a flow of nitrogen.

[0050] FIG. 14 shows the toluene desorption profiles for Ag-zeolite-β(100) before and after hydrothermal treatment at 800°C, in which a large decrease in the adsorption capacity was observed after hydrothermal treatment. FIG. 15 further shows the X-ray powder diffraction patterns for Ag-zeolite-β(100) Ag-zeolite-β(40) before and after hydrothermal treatment indicating that structural collapse occurred for Ag-zeolite-β(40).

[0051] FIG. 16 presents the results obtained for the toluene desorption profiles for SSZ-33 and Ag-SSZ-33, showing that the desorption temperature is shifted to a higher temperature in spite of its lower adsorption capacity.

[0052] FIG. 17 presents the results obtained for the toluene desorption profiles for SAPO-5 and Ag-SAPO-5, showing that the incorporation of Ag significantly reduced the adsorption capacity and the desorption temperature.

[0053] FIG. 18 presents the results obtained for the X-ray powder diffraction patterns for SSZ-33 and Ag-SSZ-33 and SAPO-5 and Ag-SAPO-5.

[0054] FIG. 19 presents the results obtained for the toluene desorption profiles for Ag exchanged SSZ-33, zeolite-β(40), and SAPO-5, showing that Ag-SSZ-33 exhibits better desorption activity (i.e., higher adsorption capacity, desorption amount and increased desorption temperature) compared with Ag-zeolite-β(40), and Ag-SAPO-5.

[0055] Table 2 further quantitatively summarizes the desorption temperatures observed for SSZ-33, zeolite-β, and SAPO zeolites, hydrothermally treated zeolites and Ag exchanged zeolites. Of particular note, the end and T<sub>max</sub> des-



orption temperatures ( $D_{\text{end}}$  and  $D_{\text{Tmax}}$ ) for SSZ-33 are superior to zeolite- $\beta$ (100).

**TABLE 2: Desorption Temperatures for zeolites, hydrothermally treated zeolites and Ag exchanged zeolites**

	sample	Amount desorbed (mg)	$D_{\text{start}}$ (°C)	$D_{\text{end}}$ (°C)	$D_{\text{Tmax}}$ (°C)
5	zeolite- $\beta$ (1590)	19.4	100	214	152
	zeolite- $\beta$ (40)	30	106	280	170,212,234
	zeolite- $\beta$ (100)	51	94	300	163
	Ag-zeolite- $\beta$ (40)	49.9	97	297	192
10	Ag-zeolite- $\beta$ (100)	52.3	94	268	157
	$\beta$ (100) HT 600°C	50.2	94	264	166
	$\beta$ (100) HT 700°C	51.6	92	262	177
	$\beta$ (100) HT 800°C	48.7	93	214	152
15	SAPO-5	48.7	101	300	160
	SAPO-11	50.6	104	242	142
	SAPO-41	31.3	106	258	163
	SAPO-5 HT 800°C	51.6			
	SAPO-5 HT 700°C	51.3	90	266	128
20	SAPO-5 HT 600°C	50.2	90	266	133
	SSZ-33	50.7	96	285	169, 188
	SSZ-33 HT	50.5	92	230	163
	SSZ-33 10K/min	50.0	51	240	135, 168
25	SSZ-33 20K/min	50.5	54	291	157, 160, 188
	SSZ-33 30K/min	50.4	53	280	169, 193
	Ag-SSZ-33	50.5	92	230	163

### Example 8

#### SEM results for hydrothermally treated zeolites

[0056] FIG. 20 presents SEM photomicrographs obtained of certain zeolites hydrothermally treated at 800°C in which particle agglomeration is evident.

### Claims

1. A method of treating exhaust gas from an internal combustion engine, said gas comprising a gaseous hydrocarbon product, the method comprising:

- contacting the exhaust gas with a CON topology molecular sieve for a time period effective to facilitate adsorption of the hydrocarbon product by the molecular sieve, such that the hydrocarbon product is at least partly adsorbed by the molecular sieve;
- passing a purge gas through the molecular sieve to remove adsorbed hydrocarbon product therefrom; and
- contacting the purge gas containing the removed hydrocarbon product with a hydrocarbon conversion catalyst, wherein

the hydrocarbon product is derived from the incomplete combustion of a hydrocarbon fuel in the internal combustion engine.

2. The method of claim 1, wherein a), b), and c) are carried out sequentially and continuously with a flowing exhaust gas.

3. The method of claim 1, wherein the CON topology molecular sieve is contained within an adsorbent material comprised of the CON topology molecular sieve.

4. The method of claim 1, wherein the exhaust gas comprises a plurality of hydrocarbon products.

5. The method of claim 1, wherein the CON topology molecular sieve is a CON topology silicate molecular sieve.
6. The method of claim 5, wherein the CON topology silicate molecular sieve comprises a framework heteroatom selected from Al, B, Ga, Fe, Zn, Mg, Co, Ge and mixtures thereof.
7. The method of claim 5, wherein the CON topology molecular sieve is selected from SSZ-33, SSZ-26, CIT-1, and mixtures thereof.
8. The method of claim 1, wherein the CON topology molecular sieve comprises SSZ-33.
9. The method of claim 1, wherein the CON topology molecular sieve contains a metal cation selected from rare earth, Group 2 metals, Groups 8-10 metals, and mixtures thereof.
10. The method of claim 1, wherein the CON topology molecular sieve contains a metal cation selected from Mn, Ca, Mg, Zn, Cd, Pt, Pd, Ni, Co, Ti, Al, Sn, Fe, Co, and mixtures thereof.
11. The method of claim 1, wherein the CON topology molecular sieve contains a metal selected from Cu, Ag, Au and mixtures thereof.
12. The method of claim 11, wherein the metal comprises Ag.
13. The method of claim 8, wherein the CON topology molecular sieve comprises SSZ-33 or Ag-SSZ-33.
14. The method of claim 1, wherein the internal combustion engine includes an exhaust system and the method is utilized to reduce the cold start emission of hydrocarbons from the exhaust system.
15. The method of claim 1, wherein the hydrocarbon product comprises a linear or branched chain non-aromatic hydrocarbon, an aromatic hydrocarbon, a polycyclic hydrocarbon, or mixtures thereof.
16. The method of claim 15, wherein the aromatic hydrocarbon includes toluene, xylene, benzene, or mixtures thereof.
17. The method of claim 1, wherein the purge gas is selected from the exhaust gas, secondary air, an inert gas, or a mixture thereof.
18. A system for treating exhaust gases from an internal combustion engine, and formed during the combustion of a hydrocarbon fuel, said system comprising:
  - an exhaust gas adsorption unit containing an adsorbent CON topology molecular sieve;
  - a catalytic converter unit containing a hydrocarbon conversion catalyst;
  - means for supplying the exhaust gas comprising a gaseous hydrocarbon product derived from the incomplete combustion of the fuel to the adsorption unit so that the hydrocarbon product is at least partly adsorbed by the molecular sieve;
  - means for transferring the hydrocarbon product from the adsorption unit to the catalytic converter unit wherein the hydrocarbon product is converted to an exhaust emission gas; and
  - means for exhausting the exhaust emission gas from the catalytic converter unit.
19. The system of claim 18, wherein the CON topology molecular sieve comprises a CON topology silicate molecular sieve.
20. The system of claim 19, wherein the CON topology silicate molecular sieve comprises a framework heteroatom selected from Al, B, Ga, Fe, Zn, Mg, Co, Ge and mixtures thereof.
21. The system of claim 19, wherein the CON topology molecular sieve is selected from SSZ-33, SSZ-26, CIT-1, and mixtures thereof.
22. The system of claim 19, wherein the CON topology molecular sieve comprises SSZ-33.
23. A method for reducing hydrocarbon emissions from an exhaust gas of an internal combustion engine, comprising

flowing the exhaust gas through the system of claim 18.

24. The method of claim 23, wherein the hydrocarbon emissions are reduced during cold start operation of the engine.

## Patentansprüche

1. Verfahren zum Behandeln von Abgas aus einem Verbrennungsmotor, wobei das Gas ein gasförmiges Kohlenwasserstoffprodukt umfasst, wobei das Verfahren umfasst:

a) Inkontaktbringen des Abgases mit einem Molekularsieb mit CON-Topologie über einen Zeitraum, der wirksam ist, Adsorption des Kohlenwasserstoffprodukts durch das Molekularsieb zu ermöglichen, so dass das Kohlenwasserstoffprodukt wenigstens teilweise von dem Molekularsieb adsorbiert wird;

b) Leiten eines Spülgases durch das Molekularsieb, um das adsorbierte Kohlenwasserstoffprodukt daraus zu entfernen; und

c) Inkontaktbringen des Spülgases, das das entfernte Kohlenwasserstoffprodukt enthält, mit einem Kohlenwasserstoffumwandlungskatalysator, wobei

das Kohlenwasserstoffprodukt aus der unvollständigen Verbrennung eines Kohlenwasserstoff-Brennstoffs in dem Verbrennungsmotor stammt.

2. Verfahren gemäß Anspruch 1, wobei a), b) und c) aufeinanderfolgend und kontinuierlich mit einem strömenden Abgas durchgeführt werden.

3. Verfahren gemäß Anspruch 1, wobei das Molekularsieb mit CON-Topologie in einem adsorbierenden Material enthalten ist, das das Molekularsieb mit CON-Topologie umfasst.

4. Verfahren gemäß Anspruch 1, wobei das Abgas eine Vielzahl von Kohlenwasserstoffprodukten umfasst.

5. Verfahren gemäß Anspruch 1, wobei das Molekularsieb mit CON-Topologie ein Silicat-Molekularsieb mit CON-Topologie ist.

6. Verfahren gemäß Anspruch 5, wobei das Silicat-Molekularsieb mit CON-Topologie ein Gerüst-Heteroatom ausgewählt aus Al, B, Ga, Fe, Zn, Mg, Co, Ge und Gemischen davon umfasst.

7. Verfahren gemäß Anspruch 5, wobei das Molekularsieb mit CON-Topologie ausgewählt ist aus SSZ-33, SSZ-26, CIT-1 und Gemischen davon.

8. Verfahren gemäß Anspruch 1, wobei das Molekularsieb mit CON-Topologie SSZ-33 umfasst.

9. Verfahren gemäß Anspruch 1, wobei das Molekularsieb mit CON-Topologie ein Metall-Kation ausgewählt aus seltenen Erden, Gruppe-2-Metallen, Gruppe-8-10-Metallen und Gemischen davon umfasst.

10. Verfahren gemäß Anspruch 1, wobei das Molekularsieb mit CON-Topologie ein Metall-Kation ausgewählt aus Mn, Ca, Mg, Zn, Cd, Pt, Pd, Ni, Co, Ti, Al, Sn, Fe, Co und Gemischen davon umfasst.

11. Verfahren gemäß Anspruch 1, wobei das Molekularsieb mit CON-Topologie ein Metall ausgewählt aus Cu, Ag, Au und Gemischen davon umfasst.

12. Verfahren gemäß Anspruch 11, wobei das Metall Ag umfasst.

13. Verfahren gemäß Anspruch 8, wobei das Molekularsieb mit CON-Topologie SSZ-33 oder Ag-SSZ-33 umfasst.

14. Verfahren gemäß Anspruch 1, wobei der Verbrennungsmotor ein Abgassystem umfasst und das Verfahren zum Verringern der Kaltstartemissionen von Kohlenwasserstoffen aus dem Abgassystem verwendet wird.

15. Verfahren gemäß Anspruch 1, wobei das Kohlenwasserstoffprodukt einen linearen oder verzweigt-kettigen nicht-aromatischen Kohlenwasserstoff, einen aromatischen Kohlenwasserstoff, einen polycyclischen Kohlenwasserstoff

oder Gemische davon umfasst.

16. Verfahren gemäß Anspruch 15, wobei der aromatische Kohlenwasserstoff Toluol, Xylol, Benzol oder Gemische davon umfasst.

17. Verfahren gemäß Anspruch 1, wobei das Spülgas ausgewählt ist aus Abgas, Sekundärluft, einem Inertgas und einem Gemisch davon.

18. System zum Behandeln von Abgasen aus einem Verbrennungsmotor, das bei der Verbrennung eines Kohlenwasserstoff-Brennstoffs entsteht, wobei das System umfasst:

eine Abgas-Adsorptionseinheit, die ein adsorbierendes Molekularsieb mit CON-Topologie enthält;  
eine katalytische Umwandlungseinheit, die einen Kohlenwasserstoffumwandlungskatalysator enthält;  
Mittel zum Zuführen des Abgases, das ein aus der unvollständigen Verbrennung des Brennstoffs stammendes gasförmiges Kohlenwasserstoffprodukt enthält, zu der Adsorptionseinheit, so dass das Kohlenwasserstoffprodukt wenigstens teilweise von dem Molekularsieb adsorbiert wird;  
Mittel zum Überführen des Kohlenwasserstoffprodukts von der Adsorptionseinheit zu der katalytischen Umwandlungseinheit, in der das Kohlenwasserstoffprodukt zu einem Auspuffemissionsgas umgewandelt wird; und  
Mittel zum Ausstoßen des Auspuffemissionsgases aus der katalytischen Umwandlungseinheit.

19. System gemäß Anspruch 18, wobei das Molekularsieb mit CON-Topologie ein Silicat-Molekularsieb mit CON-Topologie umfasst.

20. System gemäß Anspruch 19, wobei das Silicat-Molekularsieb mit CON-Topologie ein Gerüst-Heteroatom ausgewählt aus Al, B, Ga, Fe, Zn, Mg, Co, Ge und Gemischen davon umfasst.

21. System gemäß Anspruch 19, wobei das Molekularsieb mit CON-Topologie ausgewählt ist aus SSZ-33, SSZ-26, CIT-1 und Gemischen davon.

22. System gemäß Anspruch 19, wobei das Molekularsieb mit CON-Topologie SSZ-33 umfasst.

23. Verfahren zum Verringern von Kohlenwasserstoffemissionen aus einem Abgas eines Verbrennungsmotors, umfassend das Leiten des Abgases durch das System gemäß Anspruch 18.

24. Verfahren gemäß Anspruch 23, wobei die Kohlenwasserstoffemissionen während des Kaltstartbetriebs des Motors verringert werden.

## Revendications

1. Procédé de traitement des gaz d'échappement d'un moteur à combustion interne, lesdits gaz comprenant un produit d'hydrocarbure gazeux, le procédé comprenant les étapes qui consistent à :

- a) mettre les gaz d'échappement en contact avec un tamis moléculaire à topologie CON pendant une durée suffisante pour permettre l'adsorption du produit d'hydrocarbure par le tamis moléculaire, de telle sorte que le produit d'hydrocarbure soit adsorbé au moins partiellement par le tamis moléculaire,
- b) faire passer un gaz de purge à travers le tamis moléculaire pour en retirer le produit d'hydrocarbure qui s'y est adsorbé et
- c) mettre le gaz de purge contenant le produit d'hydrocarbure qui a été retiré en contact avec un catalyseur de conversion d'hydrocarbure,

le produit d'hydrocarbure provenant de la combustion incomplète d'un combustible à base d'hydrocarbure dans le moteur à combustion interne.

2. Procédé selon la revendication 1, dans lequel les étapes a), b) et c) sont conduites successivement et de manière continue sur un gaz d'échappement en écoulement.

3. Procédé selon la revendication 1, dans lequel le tamis moléculaire à topologie CON est contenu dans un matériau

adsorbant constitué du tamis moléculaire à topologie CON.

4. Procédé selon la revendication 1, dans lequel les gaz d'échappement comprennent plusieurs produits d'hydrocarbure.
5. Procédé selon la revendication 1, dans lequel le tamis moléculaire à topologie CON est un tamis moléculaire de silicate à topologie CON.
6. Procédé selon la revendication 5, dans lequel le tamis moléculaire au silicate à topologie CON comprend un hétéroatome structural sélectionné parmi Al, B, Ga, Fe, Zn, Mg, Co, Ge et leurs mélanges.
7. Procédé selon la revendication 5, dans lequel le tamis moléculaire à topologie CON est sélectionné parmi les SSZ-33, SSZ-26, CIT-1 et leurs mélanges.
8. Procédé selon la revendication 1, dans lequel le tamis moléculaire à topologie CON contient du SSZ-33.
9. Procédé selon la revendication 1, dans lequel le tamis moléculaire à topologie CON contient un cation de métal sélectionné parmi les terres rares, les métaux du groupe 2, les métaux des groupes 8 à 10 et leurs mélanges.
10. Procédé selon la revendication 1, dans lequel le tamis moléculaire à topologie CON contient un cation de métal sélectionné parmi Mn, Ca, Mg Zn, Cd, Pt, Pd, Ni, Co, Ti, Al, Sn, Fe, Co et leurs mélanges.
11. Procédé selon la revendication 1, dans lequel le tamis moléculaire à topologie CON contient un métal sélectionné parmi Cu, Ag, Au et leurs mélanges.
12. Procédé selon la revendication 11, dans lequel le métal contient Ag.
13. Procédé selon la revendication 8, dans lequel le tamis moléculaire à topologie CON comprend du SSZ-33 ou de l'Ag-SSZ-33.
14. Procédé selon la revendication 1, dans lequel le moteur à combustion interne comprend un système d'échappement, le procédé étant utilisé pour réduire l'émission d'hydrocarbures par le système d'échappement au démarrage à froid.
15. Procédé selon la revendication 1, dans lequel le produit d'hydrocarbure comprend un hydrocarbure non aromatique à chaîne linéaire ou ramifiée, un hydrocarbure aromatique, un hydrocarbure polycyclique ou leurs mélanges.
16. Procédé selon la revendication 15, dans lequel l'hydrocarbure aromatique comprend le toluène, le xylène, le benzène ou leurs mélanges.
17. Procédé selon la revendication 1, dans lequel le gaz de purge est sélectionné parmi les gaz d'échappement, de l'air secondaire, un gaz inerte ou un mélange d'entre eux.
18. Système de traitement des gaz d'échappement d'un moteur à combustion interne, formés pendant la combustion d'un combustible hydrocarbure, le système comprenant :
  - une unité d'adsorption des gaz d'échappement qui contient un tamis moléculaire adsorbant à topologie CON,
  - une unité de convertisseur catalytique contenant un catalyseur de conversion d'hydrocarbures,
  - un moyen qui délivre les gaz d'échappement contenant un produit d'hydrocarbure gazeux provenant de la combustion incomplète du combustible à l'unité d'adsorption de telle sorte que le produit d'hydrocarbure soit adsorbé au moins partiellement par le tamis moléculaire,
  - un moyen qui transfère le produit d'hydrocarbure de l'unité d'adsorption à l'unité de convertisseur catalytique dans laquelle le produit d'hydrocarbure est converti en un gaz d'émission d'échappement et
  - un moyen permettant aux gaz d'émission d'échappement de s'échapper de l'unité de convertisseur analytique.
19. Système selon la revendication 18, dans lequel le tamis moléculaire à topologie CON comprend un tamis moléculaire de silicate à topologie CON.
20. Système selon la revendication 19, dans lequel le tamis moléculaire au silicate à topologie CON comprend un

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hétéroatome structurel sélectionné parmi Al, B, Ga, Fe, Zn, Mg, Co, Ge et leurs mélanges.

21. Système selon la revendication 19, dans lequel le tamis moléculaire à topologie CON est sélectionné parmi les SSZ-33, SSZ-26, CIT-1 et leurs mélanges.

5

22. Système selon la revendication 19, dans lequel le tamis moléculaire à topologie CON contient du SSZ-33.

23. Procédé de réduction des émissions d'hydrocarbure dans les gaz d'échappement d'un moteur à combustion interne, le procédé comprenant l'étape qui consiste à faire s'écouler les gaz d'échappement à travers le système selon la revendication 18.

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24. Procédé selon la revendication 23, dans lequel les émissions d'hydrocarbure sont réduites pendant le démarrage à froid du moteur.

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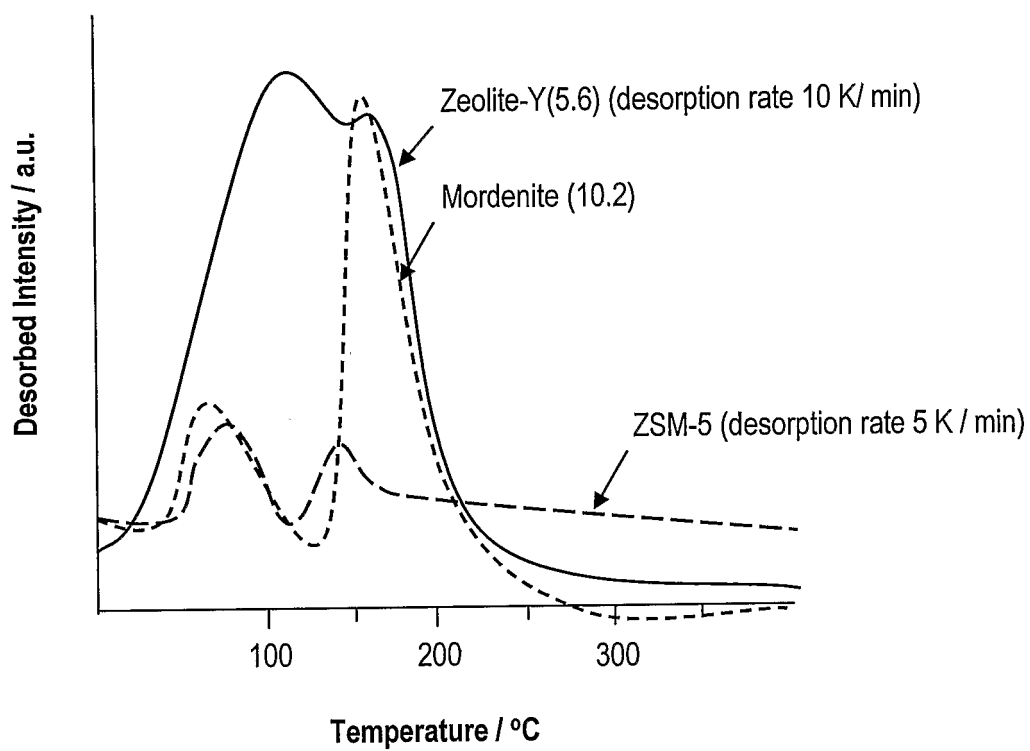
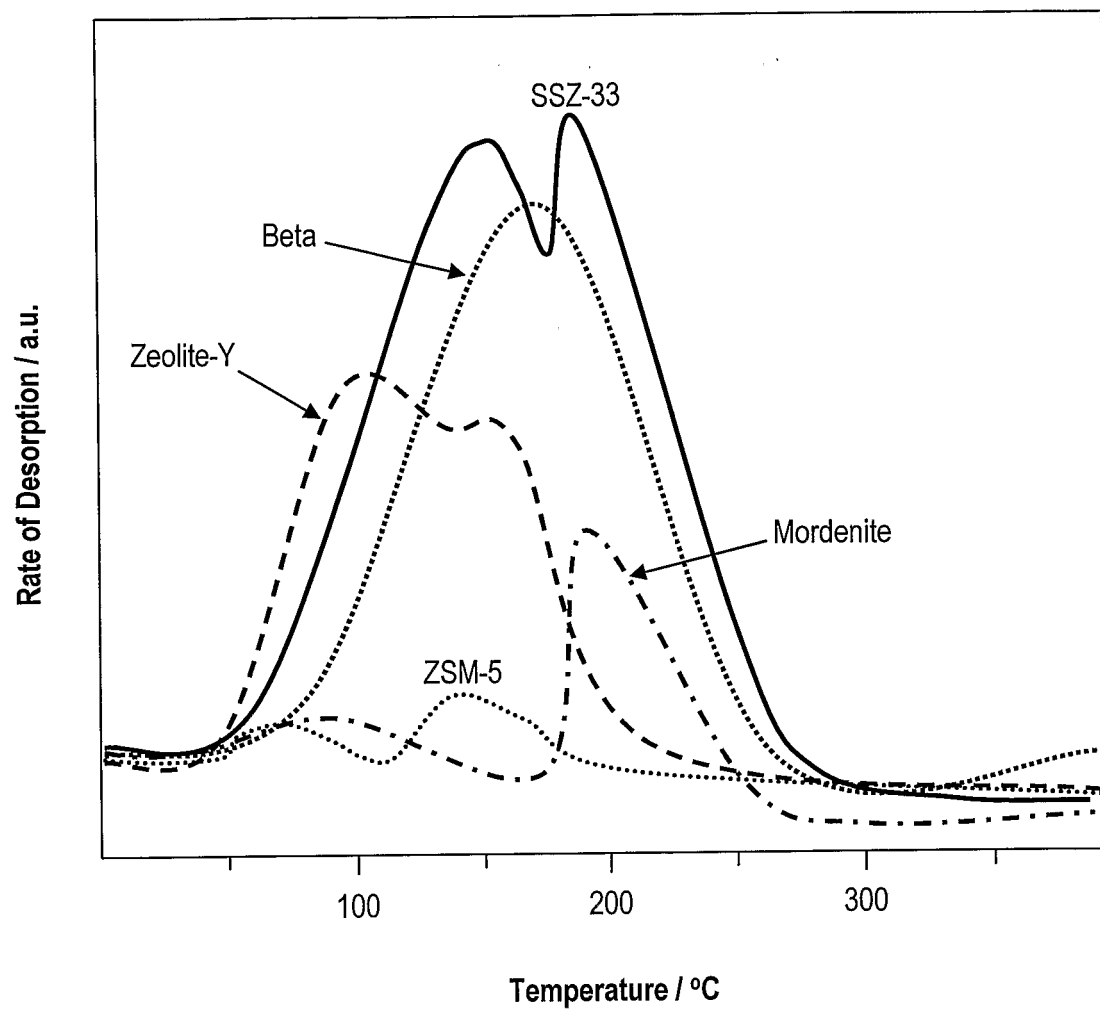
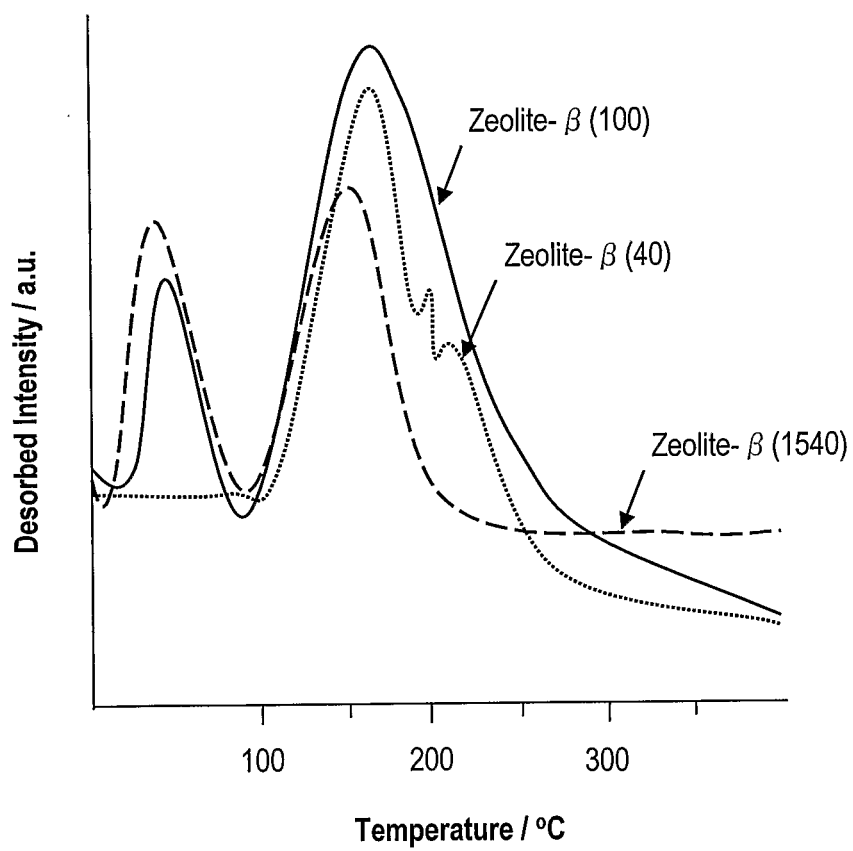
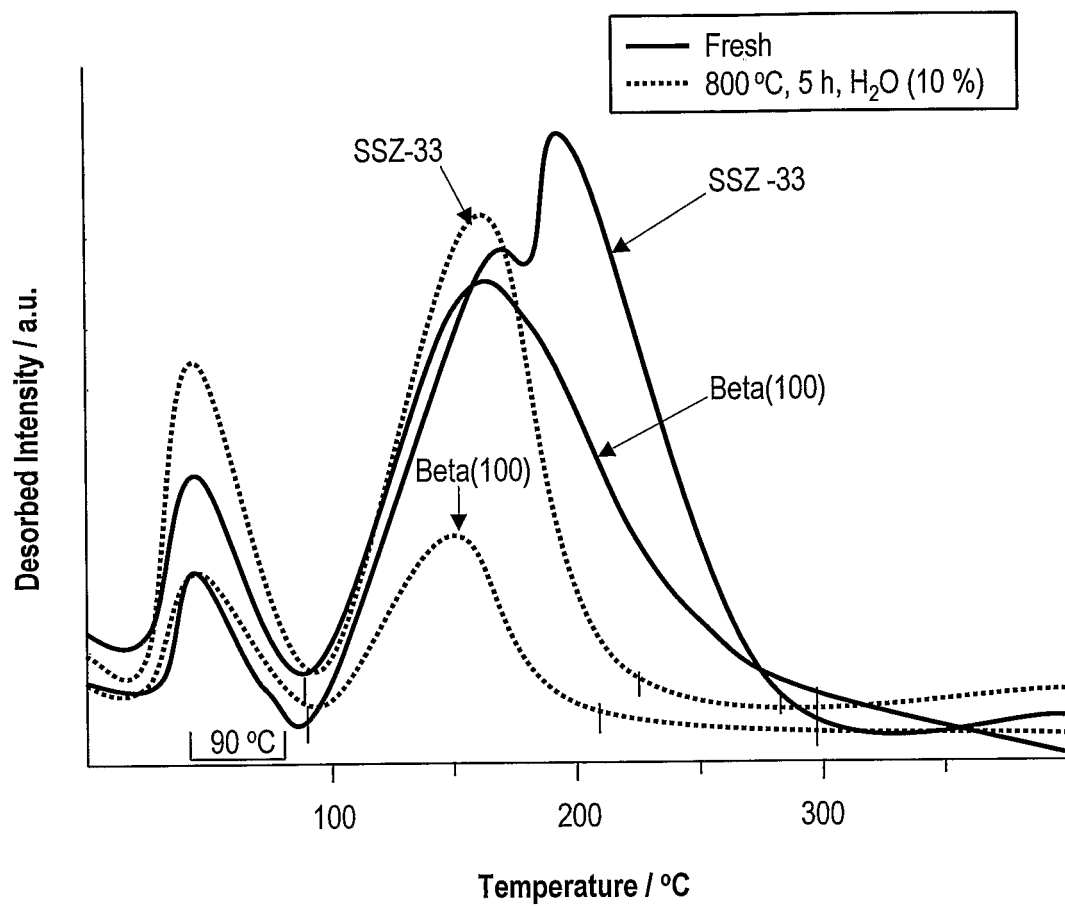


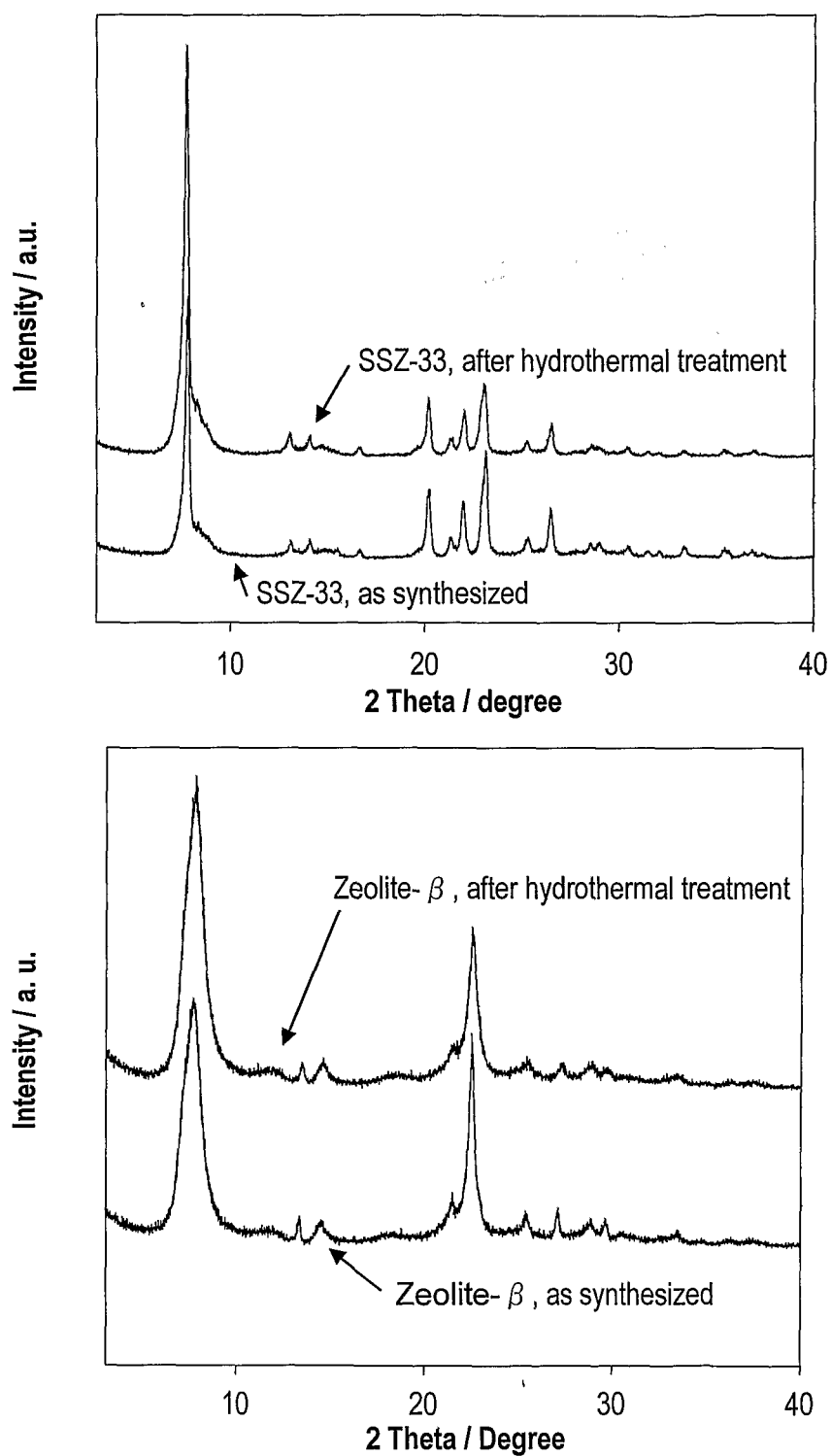
FIG. 1A

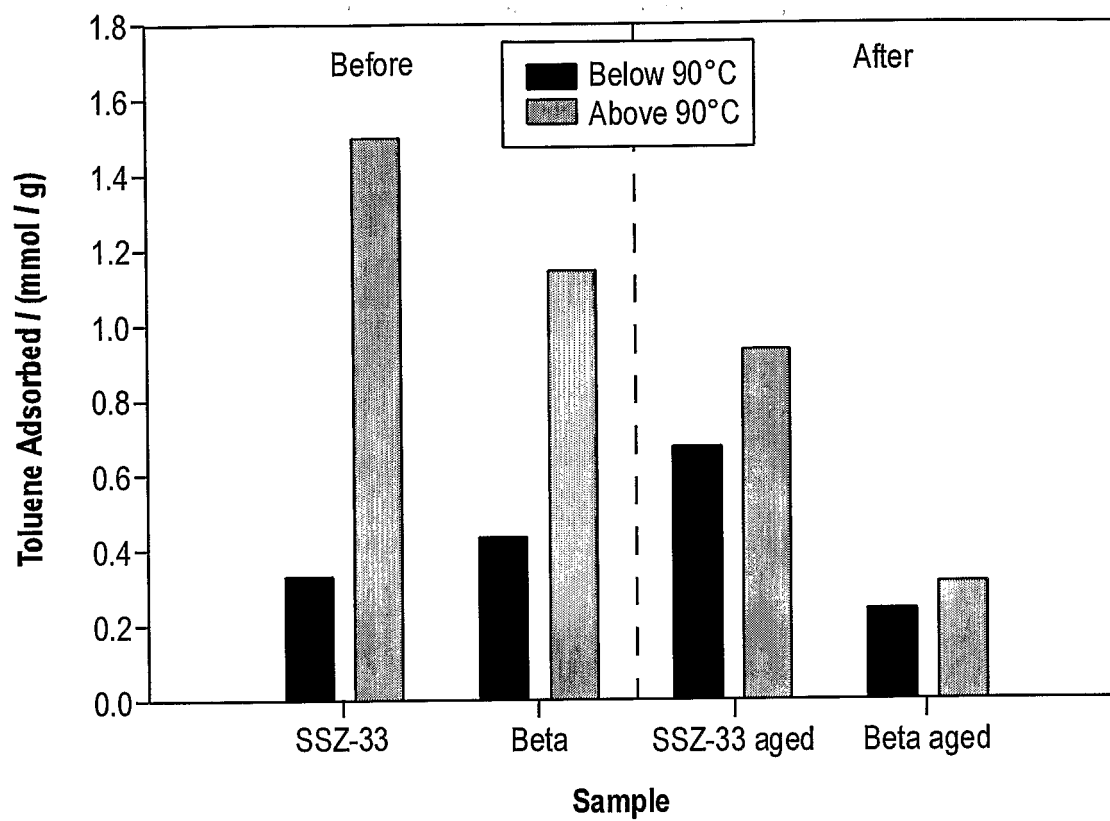
**FIG. 1B**



**FIG. 2**

**FIG. 3**

**FIG. 4**

**FIG. 5**

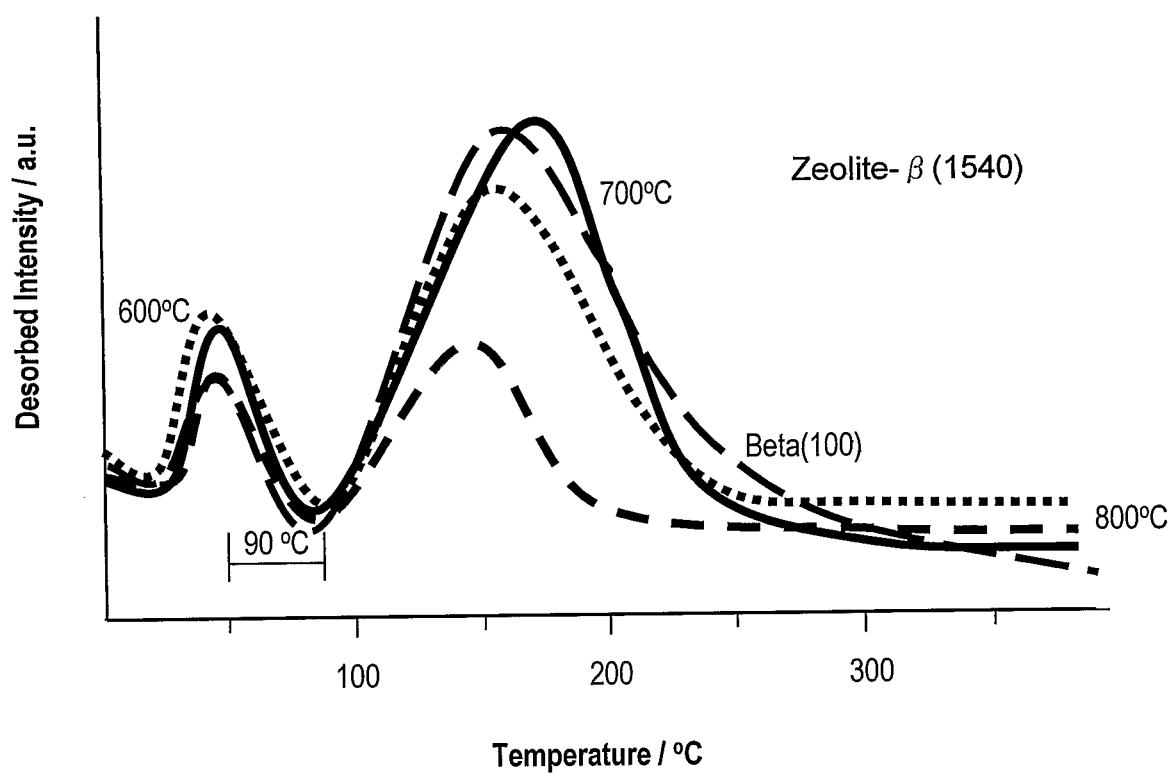


FIG. 6

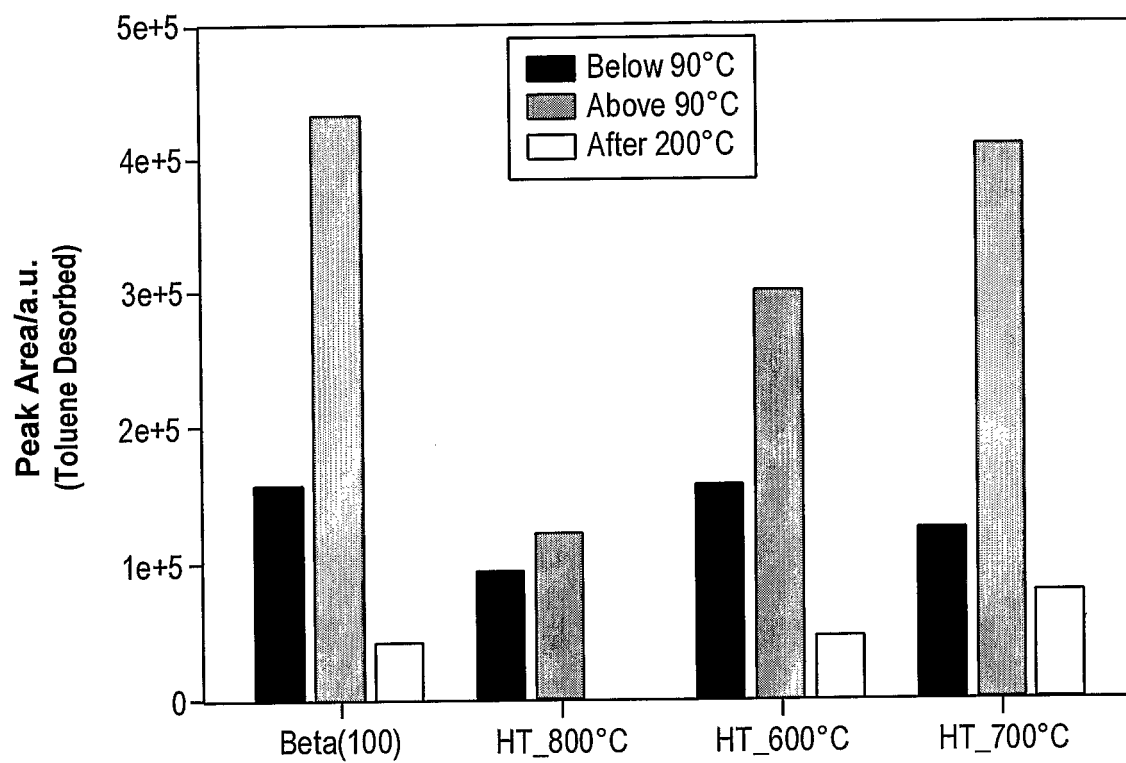
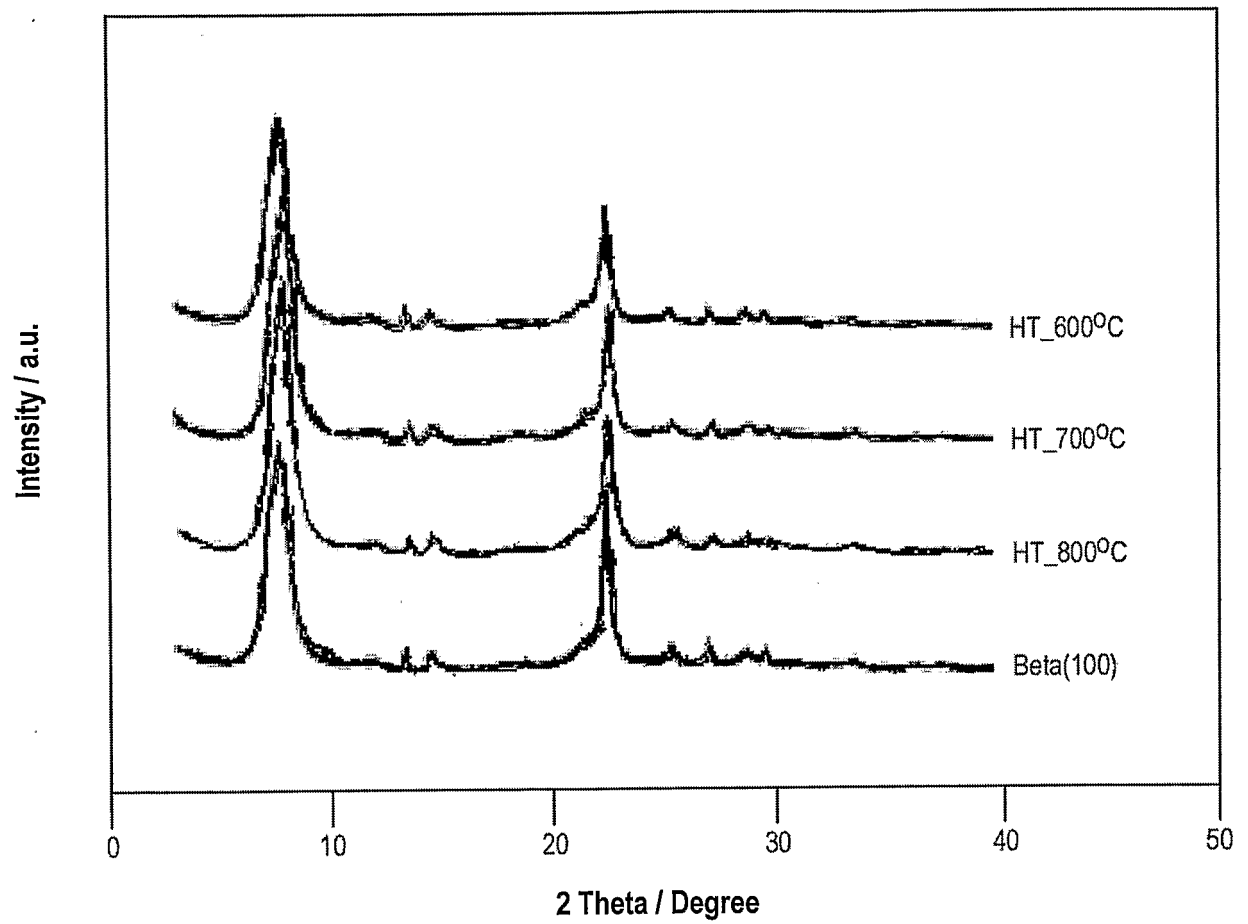


FIG. 7



**FIG. 8**

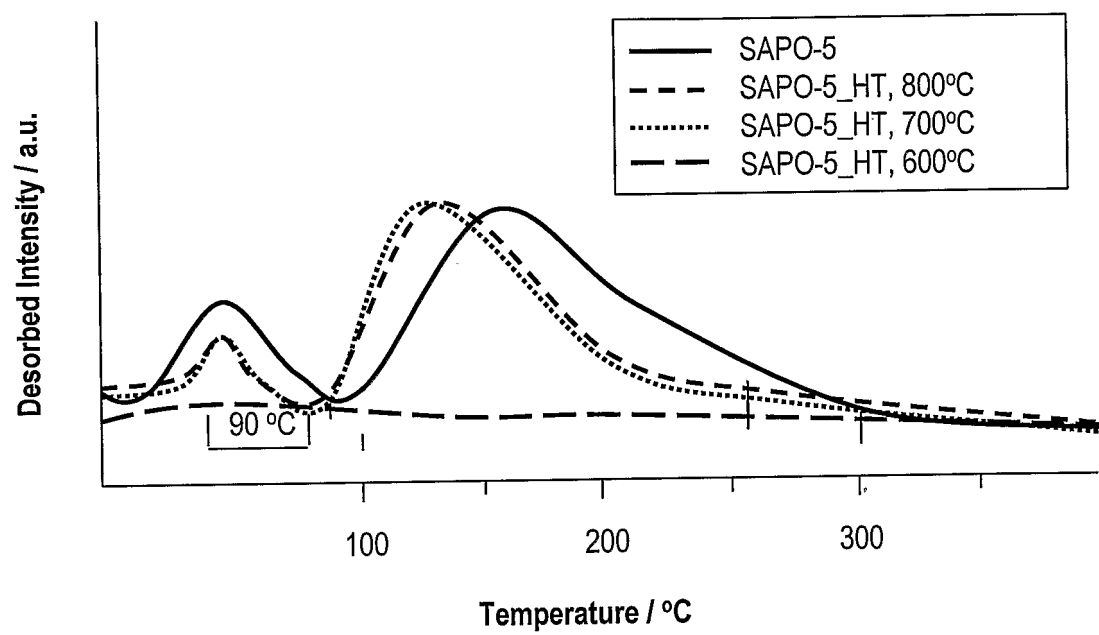
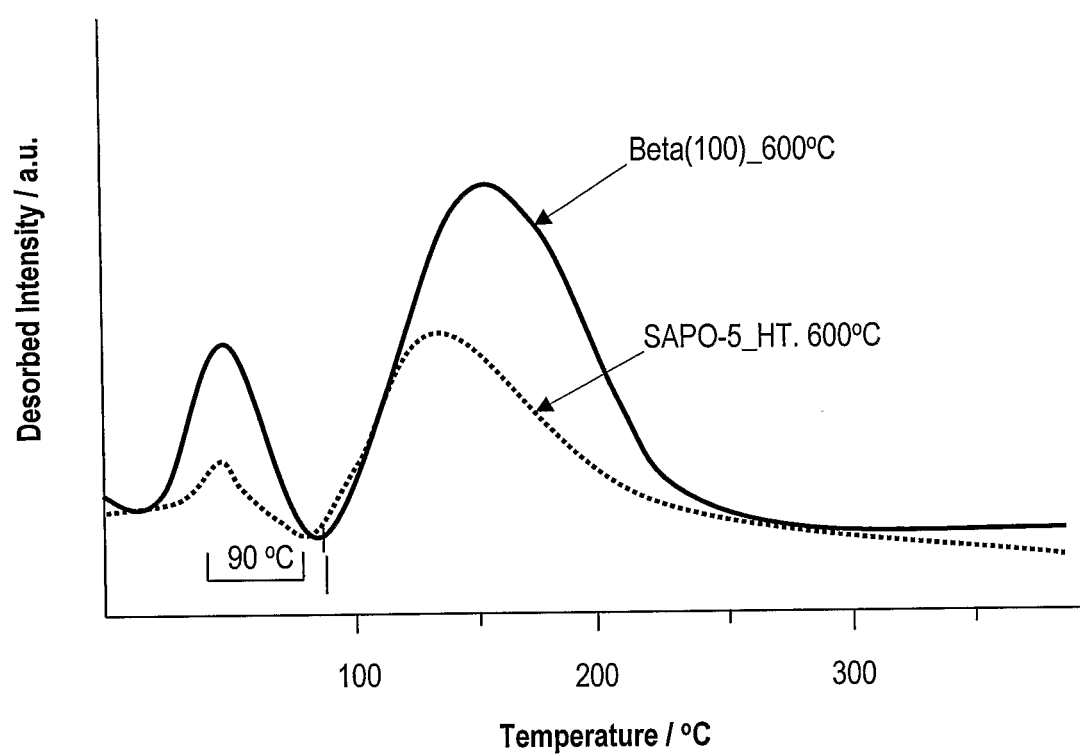


FIG. 9





**FIG. 10**

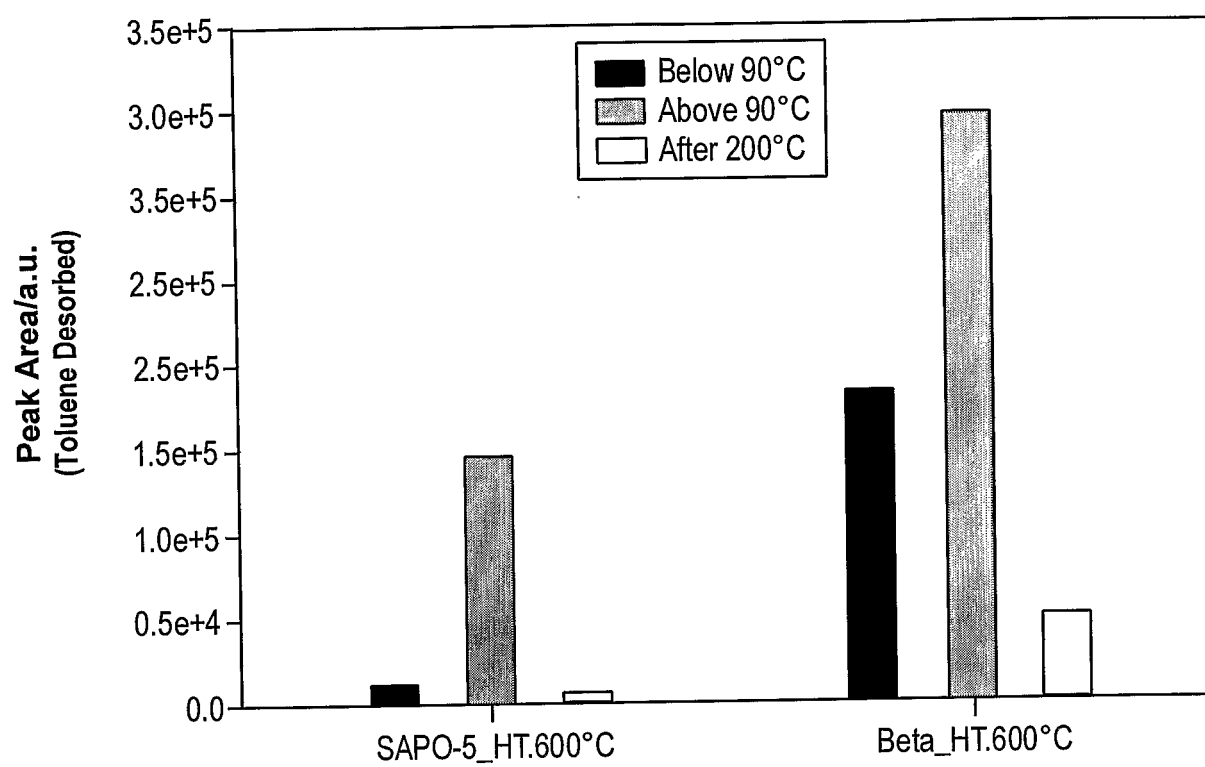
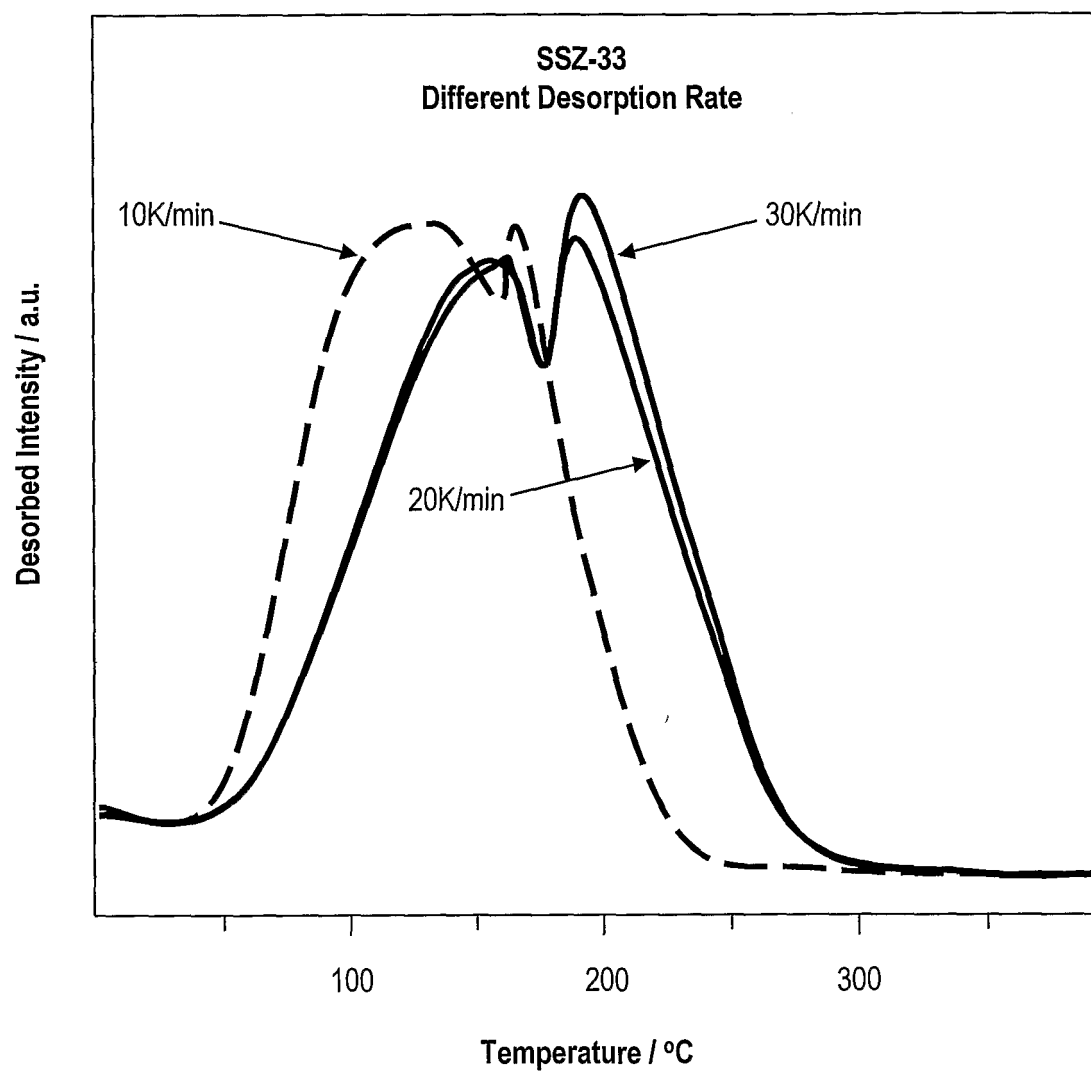


FIG. 11

**FIG. 12**

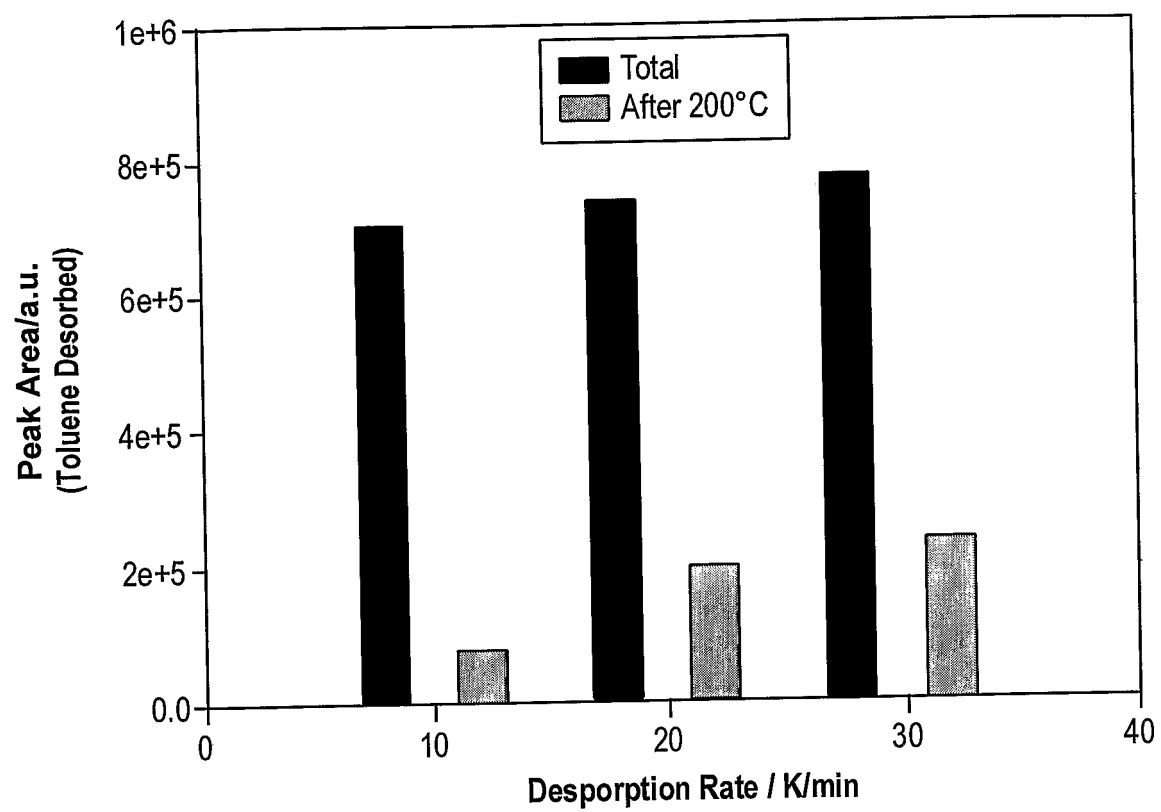


FIG. 13

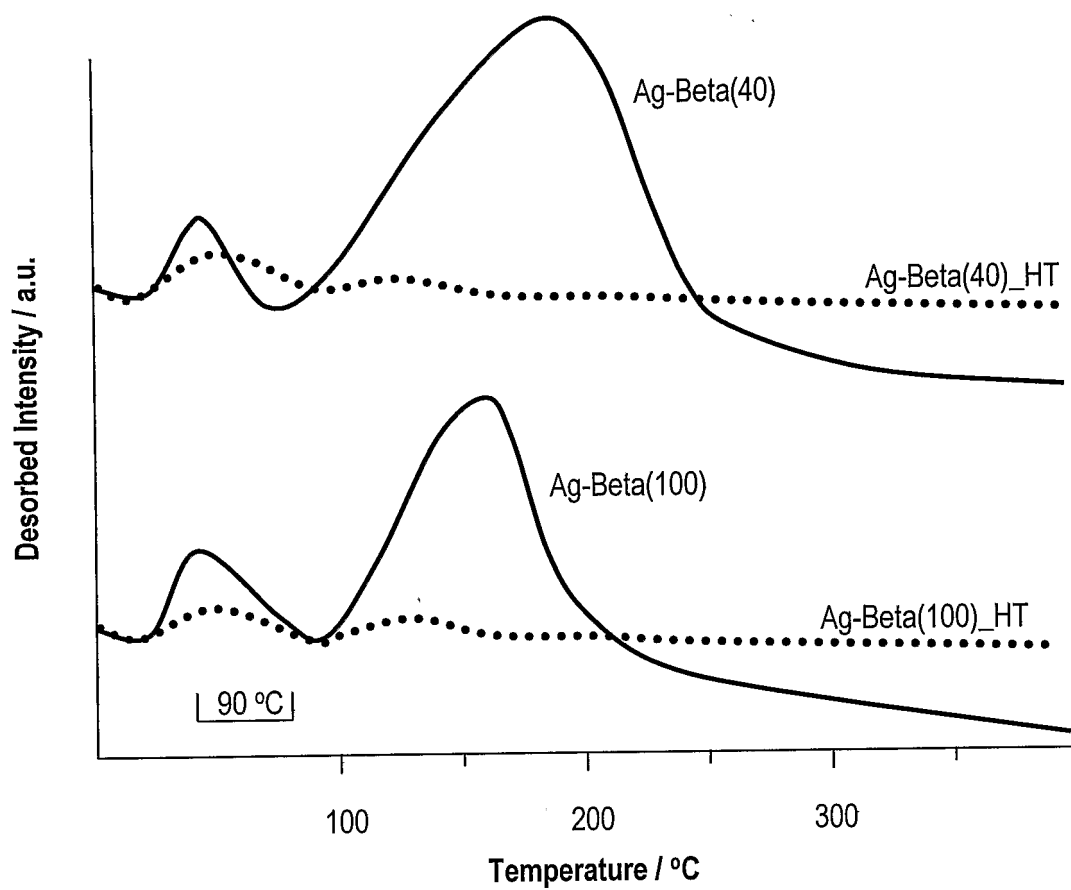


FIG. 14

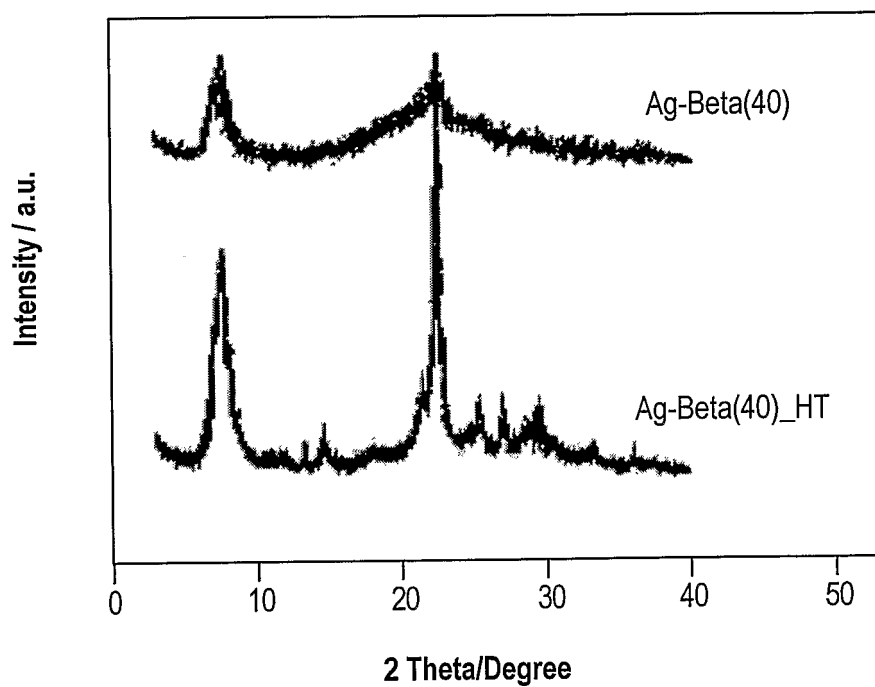
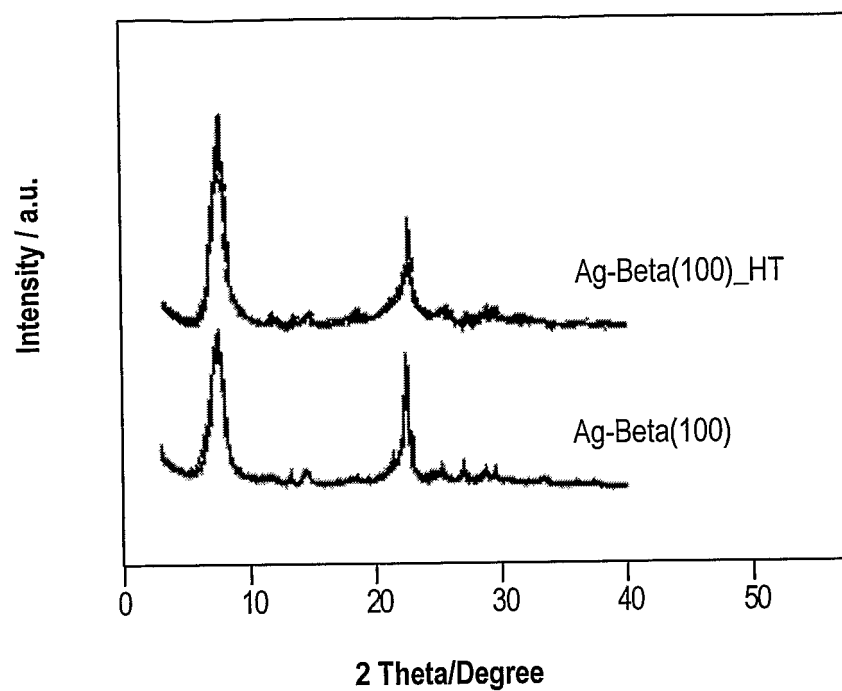


FIG. 15

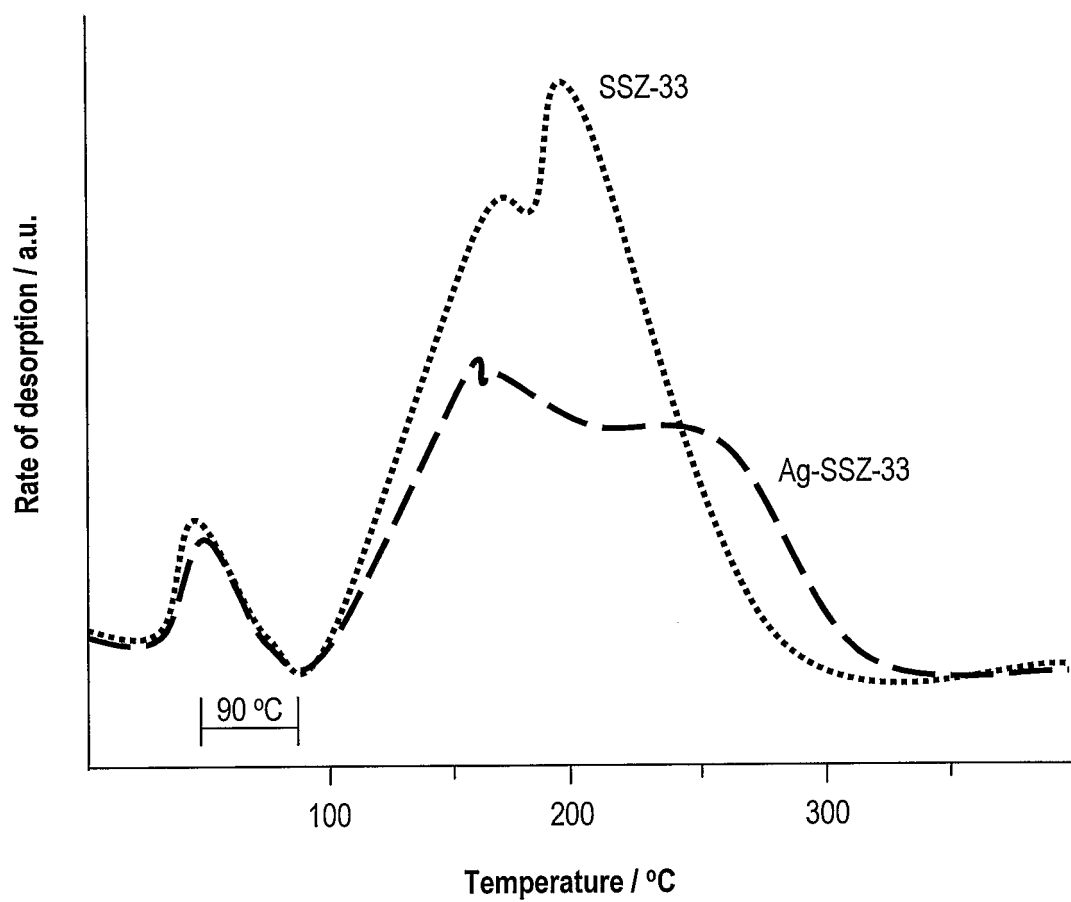
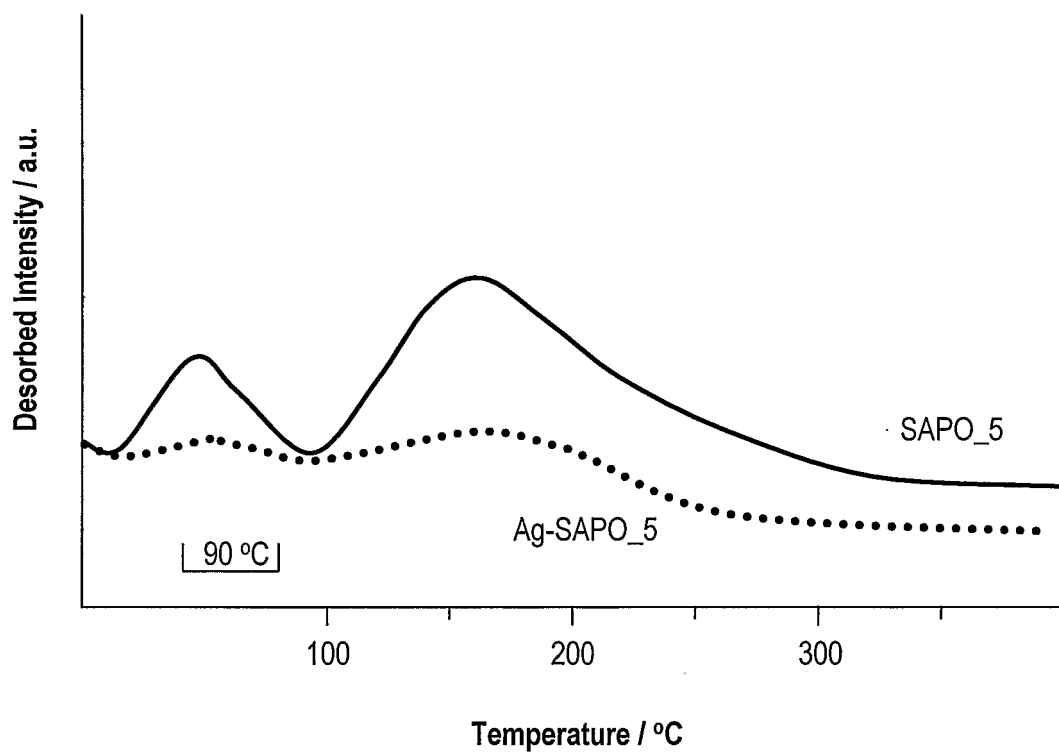


FIG. 16



**FIG. 17**



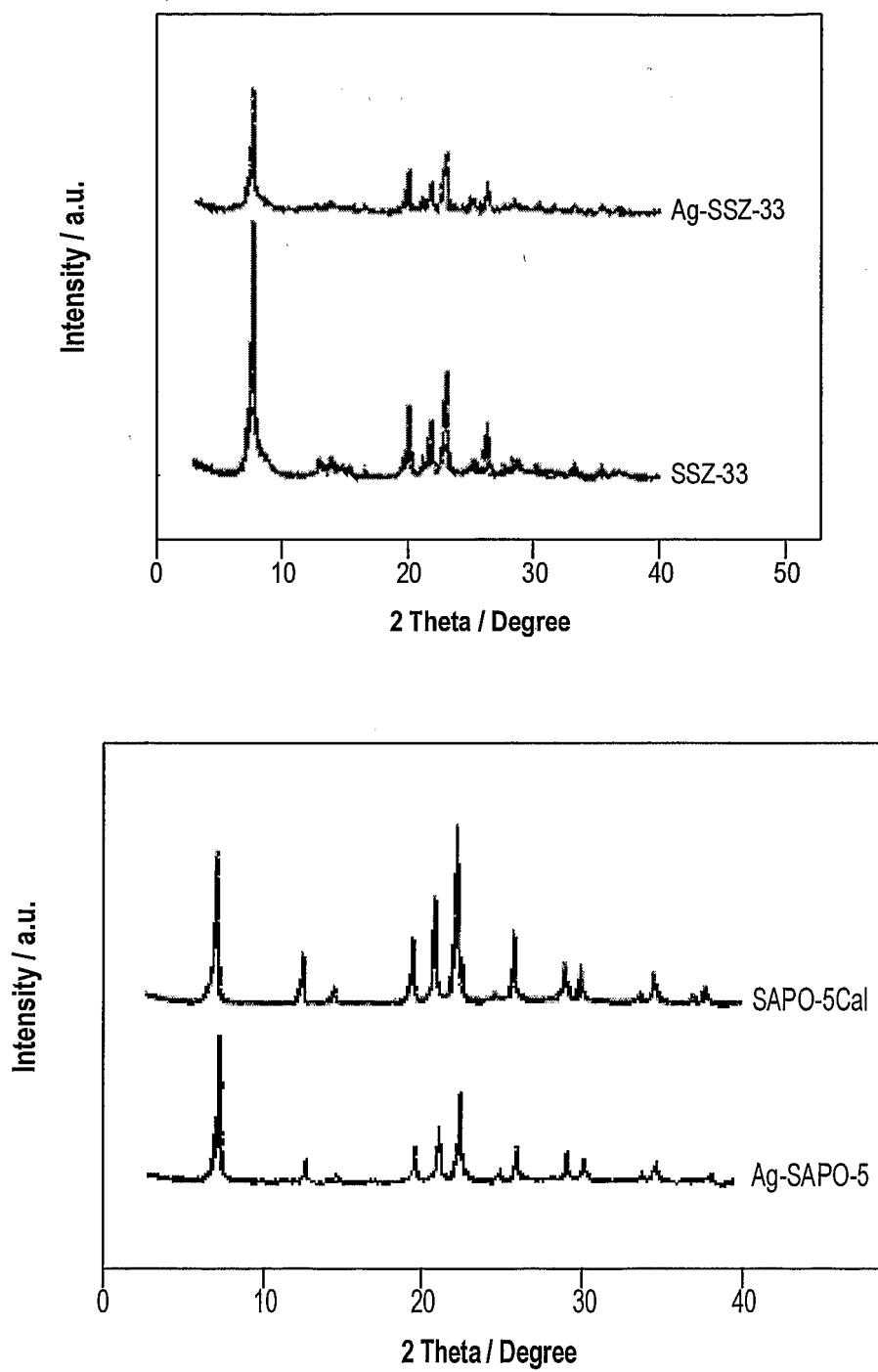


FIG. 18

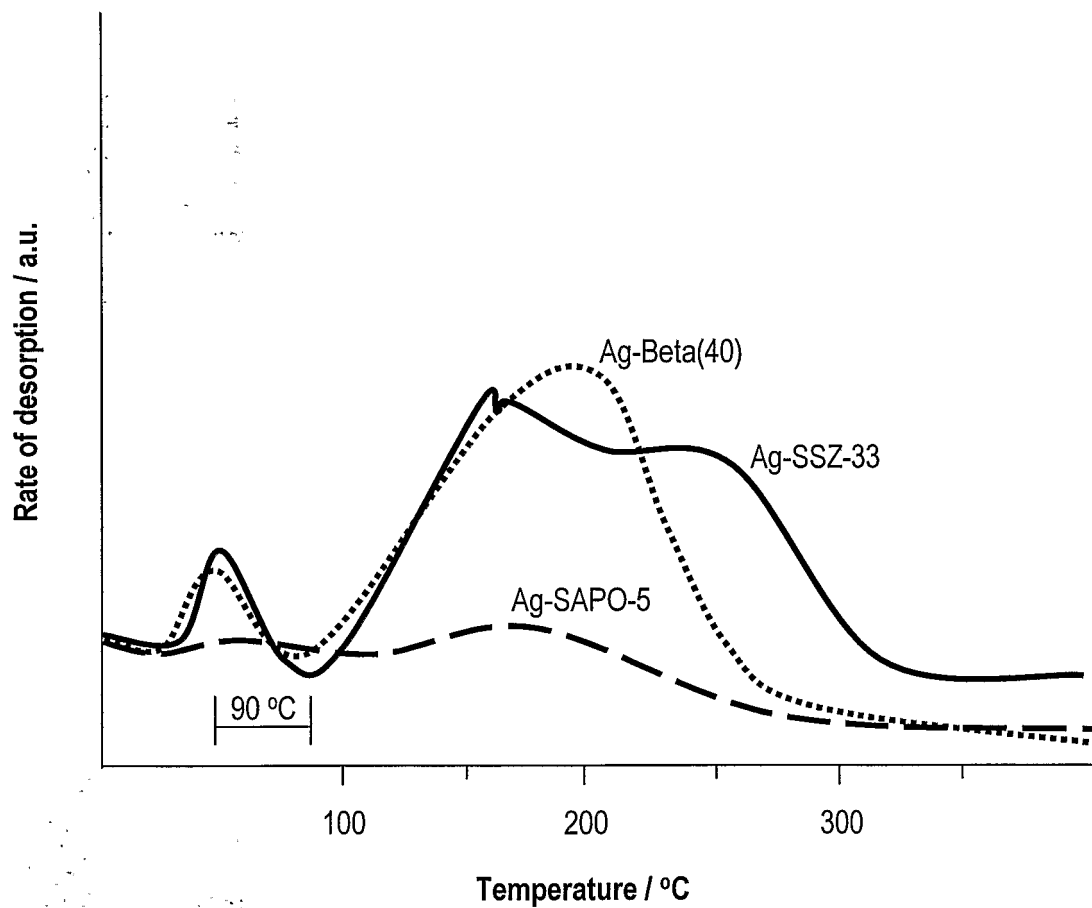
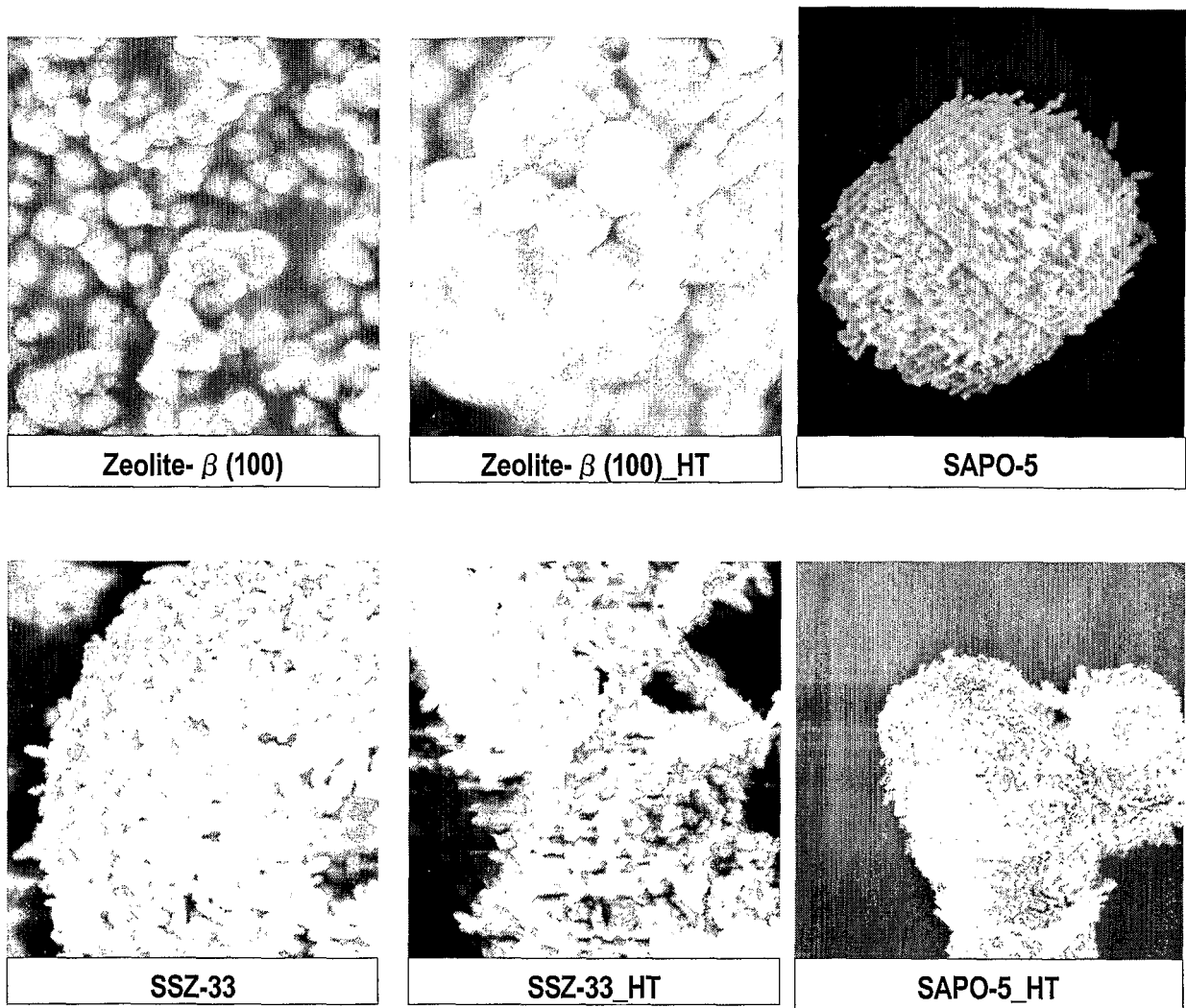


FIG. 19



**FIG. 20**

## REFERENCES CITED IN THE DESCRIPTION

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## Patent documents cited in the description

- WO 0207859 A2 [0006]
- EP 0716877 A1 [0007]
- EP 0947236 A1 [0008]
- US 4910006 A, Zones [0024] [0030]
- US 4963337 A, Zones [0024] [0030]
- US 5512267 A, Davis [0024]

## Non-patent literature cited in the description

- BURKE, N. R. ; TRIMM, D. L. ; HOWE, R. F. *Appl. Catal., B*, 2003, vol. 46, 97 [0004]
- LAFYATIS, D. S. ; ANSELL, G. P. ; BENNETT, S. C. ; FROST, J. C. ; ; MILLINGTON, P. J. ; RAJARAM, R. R. ; WALKER, A. P. ; ; BALLINGER, T. H. *Appl. Catal., B*, 1998, vol. 18, 123 [0004]
- NODA, N. ; TAKAHASHI, A ; SHIBAGAKI, Y. ; MI-ZUNO, H. *SAE Tech. Pap. Ser.*, 1998, 980423 [0004]
- CZAPLEWSKI, K. F. ; REITZ, T. L ; KIM, Y. J. ; SNURR, R. Q. *Microporous Mesoporous Mater.*, 2002, vol. 56, 55 [0004]
- JONES, C. W. ; ZONES, S. I. ; DAVIS, M. E. *Microporous and Mesoporous Materials*, 1999, vol. 28, 471 [0024]
- LIU, X. ; LAMPERT, J. K. ; ARENDARSKI, D. A. ; FARRAUTO, R. J. *Applied Catalysis B: Environmental*, 2001, vol. 35, 125 [0029]
- DARTT, C. B. ; DAVIS, M. E. *Appl. Catal., A*, 1996, vol. 143, 53 [0038]